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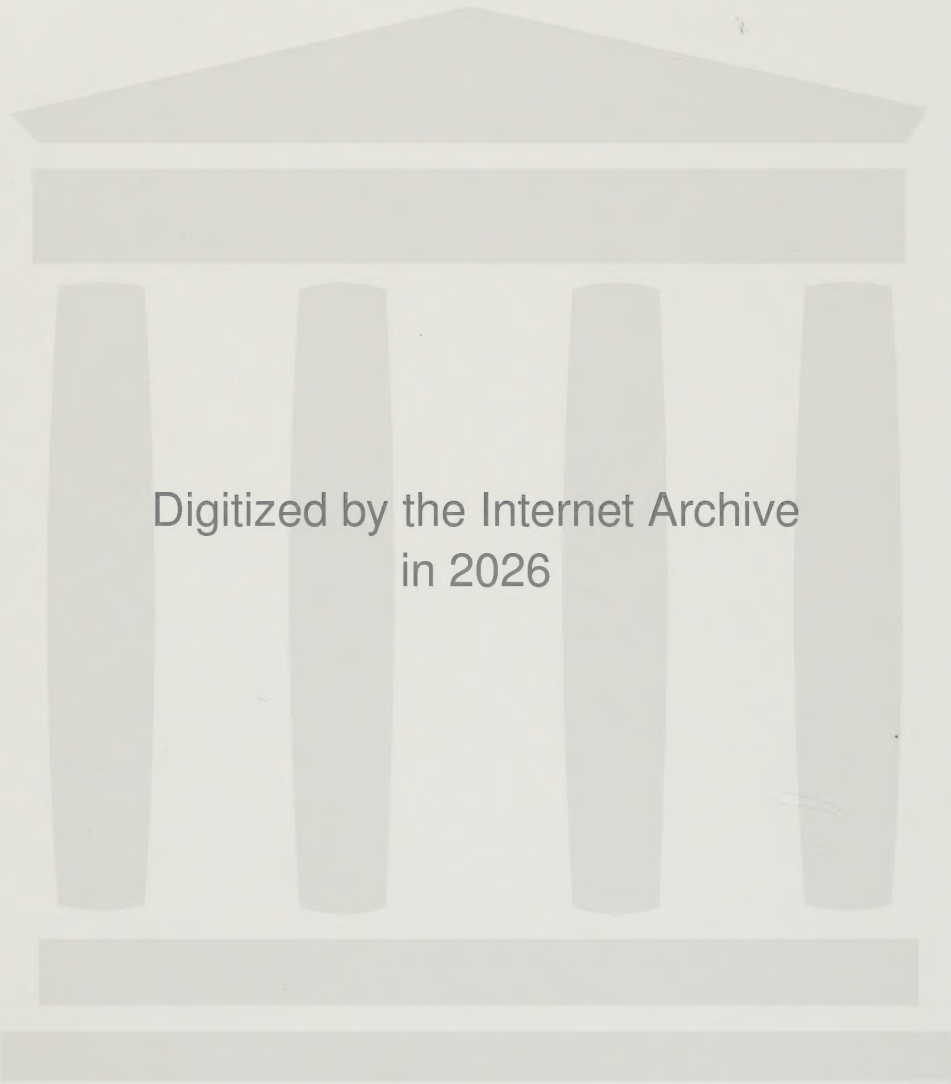
ZUMDAHL

volume two

Chemistry

sixth edition





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Chemistry

sixth edition

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UNIVERSITY OF ILLINOIS

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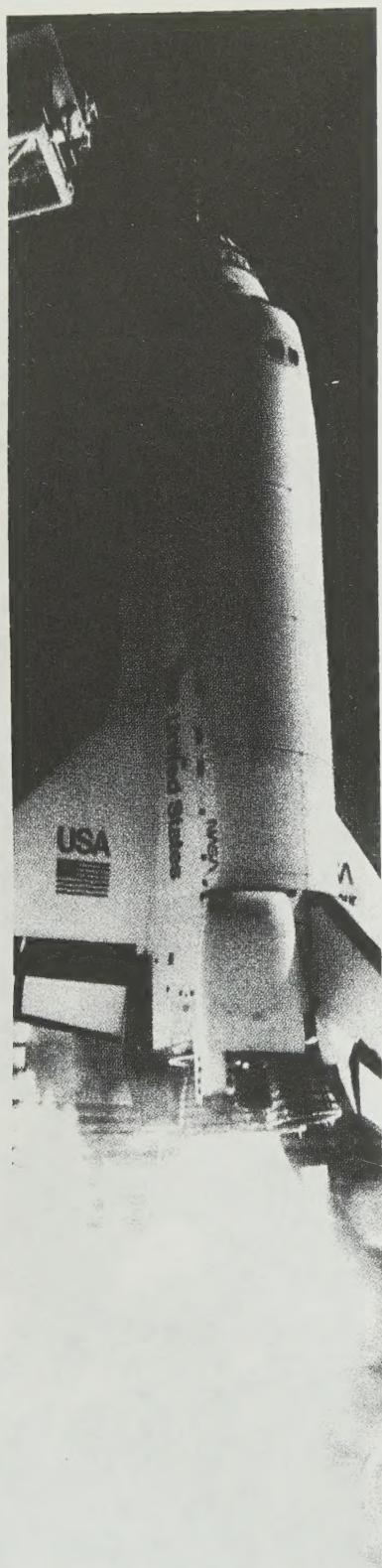
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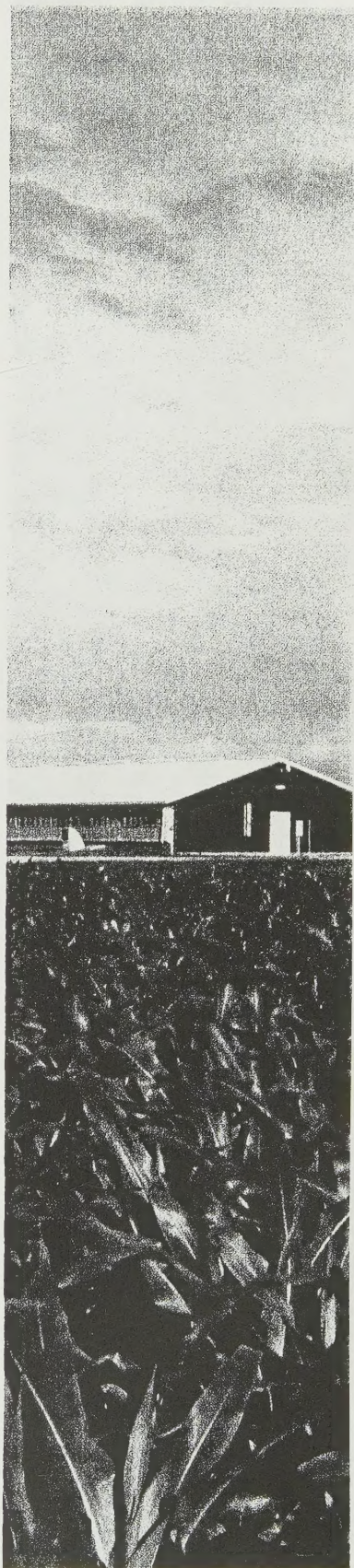
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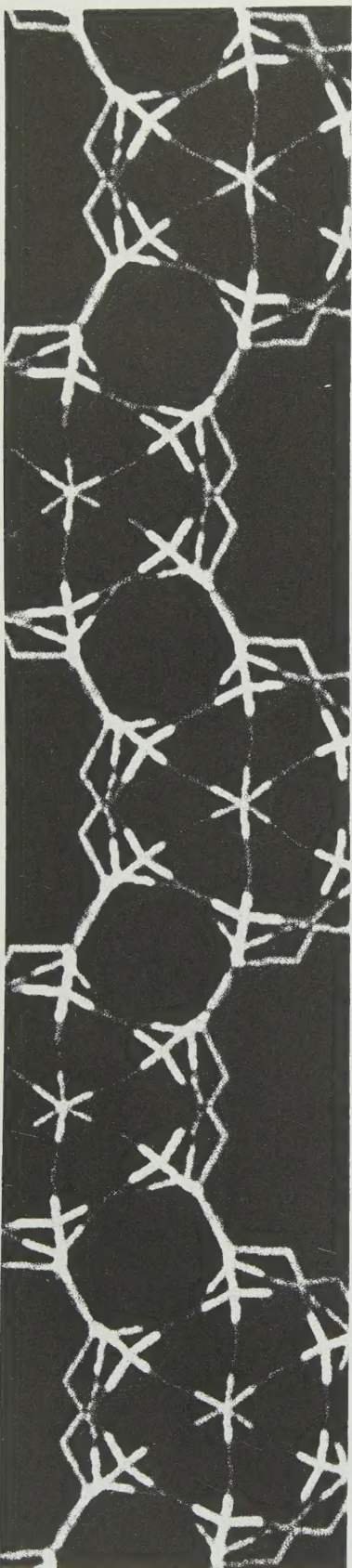
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To the Professor

Because of the positive response to the fifth edition of this text, the sixth edition of *Chemistry* continues in the same spirit: a presentation of the concepts of chemistry in a clear, interesting, and student-friendly manner. However, we have gone over every page in the fifth edition thoroughly, fine-tuning in some cases and substantially rewriting in others. In doing so, we have incorporated numerous constructive suggestions from instructors who used the previous edition.

Since visual material is especially important for learning general chemistry, which typically presents a pictorial view of chemical concepts, the art program has been revised extensively. Many new illustrations representing the microscopic world of chemistry have been added in this edition. Special illustrations and color photographs integrate descriptive chemistry with chemical principles, and many new **Chemical Impact** features emphasize practical applications of newly learned concepts.

Important Features of the Sixth Edition

- The new edition of *Chemistry* contains numerous discussions, illustrations, and exercises aimed at *overcoming common misconceptions*. It has become increasingly clear from our own teaching experience that students often struggle with chemistry because they misunderstand many of the fundamental concepts. In this text, we have gone to great lengths to provide illustrations and explanations aimed at giving students more accurate pictures of the fundamental ideas of chemistry. In particular, we have attempted to represent the microscopic world of chemistry so that students have a picture in their minds of “what the atoms and molecules are doing.” The expanded art program emphasizes this goal. Also, we have placed a larger emphasis on the qualitative understanding of concepts before quantitative problems are considered. Because using an algorithm to correctly solve a problem often masks misunderstanding—students assume they understand the material because they got the right “answer”—it is important to probe their understanding in other ways. In this vein we have included a number of conceptual questions at the end of each chapter that are intended for group discussion. It is our experience that students often learn the most when they teach each other. Students are forced to recognize their own lack of conceptual understanding when they try and fail to explain a concept to a colleague.
- With a strong *problem-solving orientation*, this text talks to the student about how to approach and solve chemical problems. We have made a strong pitch to students for using a thoughtful and logical approach rather than simply memorizing procedures. In particular, an innovative method is given for dealing with acid–base equilibria, the material the typical student finds most difficult and frustrating. The key to this approach involves first deciding what species are present in solution, then thinking about the chemical properties of these species. This method provides a general framework for approaching all types of solution equilibria.
- The text contains *almost 300 sample exercises*, with many more examples given in the discussions leading to sample exercises or used to illustrate general strategies. When a specific strategy is presented, it is summarized, and the sample exercise that follows it reinforces the step-by-step attack on the problem. In general, in approaching problem solving we emphasize understanding rather than an algorithm-based approach.
- We have presented a thorough *treatment of reactions* that occur in solution, including acid–base reactions. This material appears in Chapter 4, directly after the chapter on chemical stoichiometry, to emphasize the connection between solution reactions and chemical reactions in general. The early presentation of this material provides an opportunity to cover some interesting descriptive chemistry and also supports the lab, which typically involves a great deal of aqueous chemistry. Chapter 4 also includes oxidation–reduction reactions, because a large number of interesting and important chemical reactions involve redox processes. However, coverage of oxidation–reduction is optional at this point and depends on the needs of a specific course.
- *Descriptive chemistry* and chemical principles are thoroughly integrated in this text. Chemical models may appear sterile and confusing without the observations that stimulated their invention. On the other hand, facts without organizing principles may seem overwhelming. A combination of observations and models can make chemistry both interesting and understandable. In addition, in those chapters that deal with the chemistry of the elements systematically, we have made a continuous effort to show how properties and models correlate. Descriptive chemistry is presented in a variety of ways—as applications of the principles in separate sections, in sample exercises and exercise sets, in photographs, and in **Chemical Impact** features.
- Throughout the book a strong *emphasis on models* prevails. Coverage includes how they are constructed, how they are tested, and what we learn when they inevitably fail. Models are developed naturally, with pertinent observations always presented first to show why a particular model was invented.

- Everyday-life *applications* of chemistry that should be of interest to students taking general chemistry appear throughout the text. For example, the **Chemical Impact** “Fuel Cells for Cars” illustrates the chemistry behind cars powered by fuel cells, while “Nature Has Hot Plants” discusses several fascinating species of heat-producing plants, including the voodoo lily. Many industrial applications have also been incorporated into the text.
- A double-helix icon in the *Instructor’s Annotated Edition* highlights organic and biological examples of applications that are integrated throughout the text, in end-of-chapter problems, in exercises, or in-text discussions or examples. This feature allows instructors to quickly locate material that will be of particular interest to students in pre-medicine, biology, or other health-related fields.
- Judging from the favorable comments of instructors and students who have used the fifth edition, the text seemed to work very well in a variety of courses. We were especially pleased that *readability* was cited as a key strength when students were asked to assess the text. Thus, although the text has been fine-tuned in many areas, we have endeavored to build on the basic descriptions, strategies, analogies, and explanations that were successful in the previous editions.

New to the Sixth Edition

The sixth edition of *Chemistry* incorporates many significant improvements.

- The art program has been thoroughly revised to include many new molecular-level illustrations. New molecular-level art has been integrated into the text discussions and added to many end-of-chapter problems.
- The chapters near the end of the text have been reorganized. The chapter on nuclear chemistry has been moved from Chapter 21 to Chapter 18 in the sixth edition, and the biochemistry coverage in the fifth edition has been shortened and combined with the organic material to form a new Chapter 22 in the sixth edition. The descriptive chapters (19–21) have also been revised and updated to more accurately reflect the current teaching pedagogy.
- The end-of-chapter exercises and problems have been revised, providing approximately 20% new problems, including some that feature molecular art. End-of-chapter problems include: *In-Class Discussions Questions* to test students’ conceptual grasp of the material; *Questions* to help review important facts; *Exercises* that are paired and organized by topic; *Additional Exercises*, which are not keyed by topic; *Challenge Problems*, which require students to combine skills and problems; and *Marathon Problems*, which are the most comprehensive and challenging type of problem.
- New *Media Activities* help integrate the extensive resources in the student technology package into the general chemistry course. These activities appear following the problems listed above.
- A large number of new **Chemical Impacts** have been included in the sixth edition to continue the emphasis on up-to-date application of chemistry in the real world. These essays feature intriguing topics such as “The Chemistry of Art” and “Farming the Wind” to highlight the applications of chemistry to everyday life.
- To support the use of active learning in chemical education, we have created new PowerPoint presentations that feature in-class discussion questions called *Reacts*, chemical demonstrations, animations, and figures from the text. This material is designed to help instructors present chemistry using an interactive teaching style, which we believe is most effective in promoting student learning. An *Interactive Course Guide* includes the discussion questions and supporting information in a workbook format. The questions are repeated in the workbook (with space to record answers) so that students can focus on participation in class sessions. This guide can then be used effectively for independent student review outside of class.
- The sixth edition of *Chemistry* also features a web site specific to the text. This site includes an archive of **Chemical Impacts** from previous editions of the text as well as the current Impacts. These Impacts have links to other sites providing more information on the topic under consideration. Other areas of the site feature biographical information on the people important to the development of chemistry, links from interesting general chemical sites to sites related to each chapter in the text, information on careers relevant to the chemical sciences, flashcards to help students study important terms, and an online library of molecules.
- A very important feature accompanying the sixth edition is a new system of Interactive Online Homework, powered by *EduSpace*®, that is structured to help students learn chemistry in a conceptual way. The system is modeled on a one-to-one teacher-student problem session. When a student cannot answer a given question, instead of giving him/her the correct answer, the student receives a hint. Often the hints are in the form of a question on which the student receives feedback. The philosophy behind the electronic homework is to help students understand the material so that they can arrive at the

correct answer by their own efforts, supported by the kind of help an instructor would provide in a one-to-one tutoring session.

Another important feature of this homework system is that each student, even in a very large course, receives a unique set of tasks for each homework assignment. This is accomplished using random number generators and several versions for tasks that contain specific chemical reactions and nonnumerical concepts. Each student's work is assessed by the system and the score for each task in the assignment is recorded in the electronic gradebook for immediate access by both student and instructor. The system also encourages increased student responsibility by setting firm deadlines for assignments. From the instructor's perspective, the system encourages student study without the burden of tracking student efforts through grading. Our experience with a similar system at the University of Illinois convinces us that this new homework system represents an important breakthrough in helping students learn chemistry.

Flexibility of Topic Order

The order of topics in the text was chosen because it is preferred by the majority of instructors. However, we consciously constructed the book so that many other orders are possible. At the University of Illinois, for a two-semester sequence we use the chapters in this order: 1–6, 13–15, 7–9, 18, 21, 12, 10, 11, 16, 17, and parts of 22. Sections of Chapters 19, 20, and parts of 22 are used throughout the two semesters as appropriate. This order, chosen because of the way the laboratory is organized, is not necessarily recommended, but it illustrates the flexibility of order built into the text.

Some specific points about topic order:

- About half of chemistry courses present kinetics before equilibria; the other half present equilibria first. This text is written to accommodate either order.
- The introductory aspects of thermodynamics are presented relatively early (in Chapter 6) because of the importance of energy in various chemical processes and models, but the more subtle thermodynamic concepts are left until later (Chapter 16). These two chapters may be used together if desired.
- To make the book more flexible, the derivation of the ideal gas law from the kinetic molecular theory and quantitative analysis using spectroscopy are presented in the appendixes. Although mainstream general chemistry courses typically do not cover this material, some courses may find it appropriate. By using the optional material in the appendixes and by assigning the more difficult end-of-chapter exercises (from the additional exercises section), an instructor will find the level of the text ap-

propriate for many majors courses or for other courses requiring a more extensive coverage of these topics.

- Because some courses cover bonding using only a Lewis structure approach, orbitals are not presented in the introductory chapter on bonding (Chapter 8). In Chapter 9 both hybridization and the molecular orbital model are covered, but either or both of these topics may be omitted if desired.
- Chapter 4 can be tailored to fit the specific course involved. Used in its entirety where it stands in the book, it provides interesting examples of descriptive chemistry and supports the laboratory program. Material in this chapter can also be skipped entirely or covered at some later point, whenever appropriate. For example, the sections on oxidation and reduction can be taught with electrochemistry. Although many instructors prefer early introduction of this concept, these sections can be omitted without complication since the next few chapters do not depend on this material.

Supplements

An extensive learning and teaching package has been designed to make this book more useful to both students and instructors.

For the Student

- **Technology Guide.** Automatically packaged with all new copies of Zumdahl, *Chemistry*, this handy guide provides information and access to the technology resources available with the sixth edition. Two passkeys, one for SMARTHINKING™ online tutoring and one for the Online Homework system, are included in the guide. Passkeys are valid for 12 months from initial sign-on. A user name and password are also included for access to the student web site.

General Chemistry Interactive Student CD-ROM.

Highly interactive, offering topic summaries, conceptual enhancement, dynamic visualization, and more. Cross-platform (Macintosh/Windows) CD.

Media Activities. These end-of-chapter activities direct students to the technology resources provided to explore topics, learn concepts, and solve problems.

SMARTHINKING™ live, online tutoring

(smarthinking.com/houghton.html). Passkey required and included. This partnership between Houghton Mifflin and SMARTHINKING.com provides students with live online personalized tutoring by qualified e-structors plus asynchronous access any time.

Student web site

(chemistry.college.hmco.com/students). User name and password required and included. Includes Houghton

Mifflin's ACE self-quizzing, interactive molecules, flashcards of key terms and concepts, problems linked to the text, *Chemical Impact* boxes, and links to other useful sites, including online homework.

Houghton Mifflin's EduSpace® Interactive Online Homework system. Passkey required. The Online Homework system provides students with problems, based on the textbook, with hints and feedback to simulate a one-on-one tutoring session. Individual student progress is tracked and may be viewed, managed, and downloaded by instructors.

- *eBook*, the complete text of *Chemistry*, Sixth Edition is available in electronic format for selected eBook readers. Contact your Houghton Mifflin representative for details.
- *Study Guide*, by Paul B. Kelter of the University of North Carolina—Greensboro. Written to be a self-study aid for students, this guide includes alternate strategies for solving problems, supplemental explanations for the most difficult material, and self-tests. There are approximately 500 worked examples and 1200 practice problems (with answers), designed to give students mastery and confidence.
- *Student Solutions Manual*, by Thomas J. Hummel, Susan Arena Zumdahl, and Steven S. Zumdahl, all of the University of Illinois, Urbana, provides detailed solutions for half of the end-of-chapter exercises (designated by the blue question numbers) using the strategies emphasized in the text. To ensure the accuracy of the solutions, this supplement and the *Complete Solutions Guide* were checked independently by several instructors.
- *Interactive Course Guide*, by Donald J. DeCoste. This printed workbook can be used in lecture or recitation in conjunction with the instructor PowerPoint slides. It provides a complete set of *React* questions with space for student answers. Students can use the workbook as a self-study aid outside of class.
- *Solving Equilibrium Problems with Applications to Qualitative Analysis*, by Steven S. Zumdahl. Successfully used by thousands of students over the last ten years, this book offers thorough, step-by-step procedures for solving problems related to equilibria taking place both in the gas phase and in solution. Containing hundreds of sample exercises, test exercises with complete solutions, and end-of-chapter exercises with answers, the text utilizes the same problem-solving methods found in *Chemistry* and is an excellent source of additional drill-type problems. The last chapter presents an exploratory qualitative analysis experiment with explanations based on the principles of aqueous equilibria.
- *Experimental Chemistry*, Sixth Edition, by James F. Hall of the University of Massachusetts—Lowell, provides an

extensively revised laboratory program compatible with the text. The 48 experiments present a wide variety of chemistry, and many experiments offer choices of procedures. Safety is strongly emphasized throughout the program.

For the Instructor

- *HM ClassPrep™ with HMTesing™ Version 6.0 CD-ROM* includes everything an instructor needs to develop lectures: PowerPoint slides with lecture outlines; all text figures, tables, and virtually all photos; as well as *Instructor's Resource Guide* (pdf format); *Test Bank* (MS Word files of the printed *Test Bank*); and animation and video files. It also includes a series of large-format animations and videos for use in the classroom.
- *HM Testing Version 6.0* combines a flexible test-editing program with a comprehensive gradebook function for easy administration and tracking. It enables instructors to administer tests via network server or the web. The *HM Testing* database can produce multiple-choice, true/false, fill-in-the-blank, and essay tests. Questions can be customized based on the chapter being covered, the question format, level of difficulty, and specific topics. *HM Testing* provides high security for accessing test questions and grades. Cross-platform for Macintosh and Windows.
- *Instructor web site at college.hmco.com* is a text-specific site designed for instructors that offers access to all student web site resources, downloadable PowerPoint slides for use in lectures, additional classroom resources, and relevant links.
- *Course Management Software* is available through *WebCT* and *Blackboard.com*. These two distributed learning systems allow instructors to create a virtual classroom without any knowledge of HTML. Features include: assessment tools, a gradebook, online file exchange between instructors and students, online syllabi, and course descriptions. The customized *Chemistry* cartridges feature quizzes, study materials, and exercises related to the text.
- *Complete Solutions Guide*, by Thomas J. Hummel, Susan Arena Zumdahl, and Steven S. Zumdahl, presents detailed solutions for all of the end-of-chapter exercises in the text for the convenience of faculty and staff involved in instruction and for instructors who wish their students to have solutions for all exercises. Departmental approval is required for the sale of the *Complete Solutions Guide* to students.
- *Instructor's Resource Guide*, by Donald J. DeCoste, includes suggestions for alternative orders of topics, solutions to the Marathon Problems, suggested responses to the In-Class Discussion Questions, amplification of strategies used in various chapters, suggested sources

of additional information, answers to *Reacts*, and a section on notes for teaching assistants.

- *Lecture Demonstration Guide*, by Fred Jurgens of the University of Wisconsin—Madison, lists the sources for over 750 classroom demonstrations that can be used in general chemistry courses. Icons in the margins of the *Instructor's Annotated Edition* of the text key the demonstrations to their corresponding text discussions.
- *Instructor's Resource Guide for Experimental Chemistry*, Sixth Edition, by James F. Hall, contains tips including hints on running experiments, approximate times for each experiment, and answers to all prelab and postlab questions posed in the laboratory guide.
- *Bibliobase* (www.bibliobase.com) allows instructors to create a completely customized lab manual by mixing and matching from 88 general chemistry labs—including all the labs from *Experimental Chemistry*—and 56 labs for the course in general, organic, and biochemistry. At the web site, instructors search through the database of labs, make their selections, organize the sequence of the manual, and submit their order via the Internet. Customized, printed, and bound lab manuals are delivered to the bookstore within weeks.
- *Test Item File*, by Steven S. Zumdahl, Susan Arena Zumdahl, and Donald J. DeCoste (available to adopters), offers a printed version of more than 2000 exam questions, 10 percent of which are new to this edition, referenced to the appropriate text section. Questions are in multiple-choice, open-ended, and true-false formats.
- *Transparencies*, in a full-color set of 255, are available to adopters of the sixth edition of the text.
- *Houghton Mifflin Chemistry Videodiscs Volumes I and II* contain video clips of lecture demonstrations, animations of important chemical processes and concepts, and still images from the text that can be used in classroom presentations. Both discs are available free to adopters of the sixth edition.
- *Houghton Mifflin Videotapes Series A, B, C, and D* provide over 100 lecture demonstrations performed by John Luoma, Cleveland State University; John J. Fortman and Rubin Battino, Wright State University; Patricia L. Samuel, Boston University; and Paul Kelter, University of North Carolina—Greensboro.
- *General Chemistry DVD*. This disc contains the animations on the *Chemistry Video and Animations* CD-ROM and on the *Lecture Hall Animations* CD-ROM, plus the videos on videotape Series C.

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To the Student

The major purpose of this book, of course, is to help you learn chemistry. However, this main thrust is closely linked to two other goals: to show how important and how interesting the subject is, and to show how to think like a chemist. To solve complicated problems the chemist uses logic, trial and error, intuition, and, above all, patience. A chemist is used to being wrong. The important thing is to learn from a mistake, recheck assumptions, and try again. A chemist thrives on puzzles that seem to defy solutions.

Many of you using this text do not plan to be practicing chemists. However, the nonchemist can benefit from the chemist's attitude. Problem solving is important in all professions and in all walks of life. The techniques you will learn from this book will serve you well in any career you choose. Thus, we believe that the study of chemistry has much to offer the nonmajor, including an understanding of many fascinating and important phenomena and a chance to hone problem-solving skills.

This book attempts to present chemistry in a manner that is sensible to the novice. Chemistry is not the result of an inspired vision. It is the product of countless observations and many attempts, using logic and trial and error, to account for these observations. In this book the concepts are developed in a natural way: The observations come first and then models are constructed to explain the observed behavior.

Models are a major focus in this book. The uses and limitations of models are emphasized, and science is treated as a human activity, subject to all the normal human foibles. Mistakes are discussed as well as successes.

A central theme of this book is a thoughtful, systematic approach to problem solving. Learning encompasses much more than simply memorizing facts. Truly educated people use their factual knowledge as a starting point—a base for creative approaches to solving problems.

Read through the material in the text carefully. For most concepts, illustrations or photos will help you visualize what is going on. To further help you visualize concepts by using animations and videos, we have packaged a CD-ROM, *General Chemistry: Interactive*, with your text. CD icons in the text margin signal that there is companion material available on the CD.

Often a given type of problem is “walked through” in the text before the corresponding sample exercises appear. Strategies for solving problems are given throughout the text.

Thoroughly examine the sample exercises and the problem-solving strategies. The strategies summarize the approach taken in the text; the sample exercises follow the strategies step-by-step. Schematics in Chapter 15 also illustrate the logical pathways to solving aqueous equilibrium problems.

Throughout the text, we have used margin notes to highlight key points, to comment on an application of the text material, or to reference material in other parts of the book. **Chemical Impact**, the boxed feature that appears frequently throughout the text, discusses especially interesting applications of chemistry to the everyday world.

Each chapter has a summary and key terms list for review, and the glossary gives a quick reference for definitions.

Learning chemistry requires working the end-of-chapter exercises assigned by your professor. Answers to exercises denoted by blue question numbers are in the back of the book, and complete solutions to those exercises are in the *Partial Solutions Guide*. To help you assess your level of proficiency, the *student web site* (www.college.hmco.com) offers quizzes and electronic homework assignments that feature instant feedback.

The *Study Guide* contains extra practice problems and many worked examples. The supplement, *Solving Equilibrium Problems with Applications to Qualitative Analysis*, reinforces in great detail the text's step-by-step approach to solving equilibrium problems and contains many worked examples and self-quiz questions.

It is very important to use the exercises and electronic homework assignments to your best advantage. Your main goal should not be to simply get the correct answer but to *understand the process* for getting the answer. Memorizing the solutions for specific problems is not a very good way to prepare for an exam. There are too many pigeonholes required to cover every possible problem type. Look within the problem for the solution. Use the concepts you have learned along with a systematic, logical approach to find the solution. Learn to trust yourself to think it out. You will make mistakes, but the important thing is to learn from these errors. The only way to gain confidence is to do lots of practice problems and use these to diagnose your weaknesses.

Be patient and thoughtful and work hard to understand rather than simply memorize. We wish you an interesting and satisfying year.

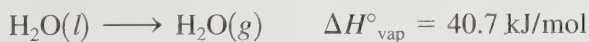
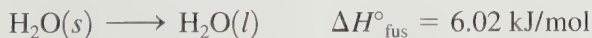
Liquids and Solids

You have only to think about water to appreciate how different the three states of matter are. Flying, swimming, and ice skating are all done in contact with water in its various forms. Clearly, the arrangements of the water molecules must be significantly different in its gas, liquid, and solid forms.

In Chapter 5 we saw that a gas can be pictured as a substance whose component particles are far apart, are in rapid random motion, and exert relatively small forces on each other. The kinetic molecular model was constructed to account for the ideal behavior that most gases approach at high temperatures and low pressures.

Solids are obviously very different from gases. A gas has low density and high compressibility and completely fills its container. Solids have much greater densities, are compressible only to a very slight extent, and are rigid—a solid maintains its shape irrespective of its container. These properties indicate that the components of a solid are close together and exert large attractive forces on each other.

The properties of liquids lie somewhere between those of solids and gases but not midway between, as can be seen from some of the properties of the three states of water. For example, compare the enthalpy change for the melting of ice at 0°C (the heat of fusion) with that for vaporizing liquid water at 100°C (the heat of vaporization):



These values show a much greater change in structure in going from the liquid to the gaseous state than in going from the solid to the liquid state. This

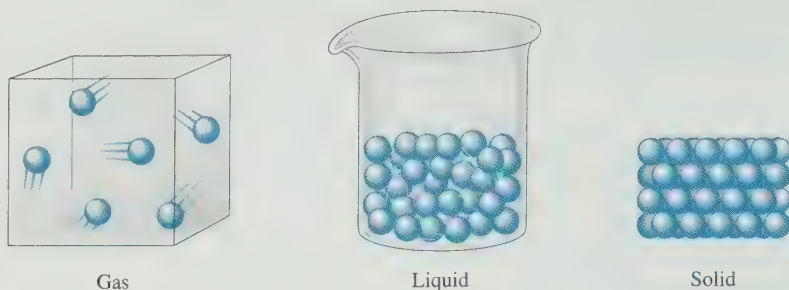
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Aerial view of the Prismatic Pool in Yellowstone National Park shows steam rising from this thermal pool.

TABLE 10.1**Densities of the Three States of Water**

State	Density (g/cm ³)
Solid (0°C, 1 atm)	0.9168
Liquid (25°C, 1 atm)	0.9971
Gas (400°C, 1 atm)	3.26×10^{-4}

**FIGURE 10.1**

Schematic representations of the three states of matter.

suggests that there are extensive attractive forces among the molecules in liquid water, similar to but not as strong as those in the solid state.

The relative similarity of the liquid and solid states also can be seen in the densities of the three states of water. As shown in Table 10.1, the densities for liquid and solid water are quite close.* Compressibilities also can be used to explore the relationship among water's states. At 25°C, the density of liquid water changes from 0.99707 g/cm³ at a pressure of 1 atm to 1.046 g/cm³ at 1065 atm. Given the large change in pressure, this is a very small variation in the density. Ice also shows little variation in density with increased pressure. On the other hand, at 400°C, the density of gaseous water changes from 3.26×10^{-4} g/cm³ at 1 atm pressure to 0.157 g/cm³ at 242 atm—a huge variation.

The conclusion is clear. The liquid and solid states show many similarities and are strikingly different from the gaseous state, as shown schematically in Fig. 10.1. We must bear this in mind as we develop models for the structures of solids and liquids.

We will proceed in our study of liquids and solids by first considering the properties and structures of liquids and solids. Then we will consider the changes in state that occur between solid and liquid, liquid and gas, and solid and gas.



Understanding Concepts:
Intermolecular Forces

10.1 Intermolecular Forces

In Chapters 8 and 9 we saw that atoms can form stable units called *molecules* by sharing electrons. This is called *intramolecular* (within the molecule) *bonding*. In this chapter we consider the properties of the **condensed states** of matter (liquids and solids) and the forces that cause the aggregation of the components of a substance to form a liquid or a solid. These forces may involve covalent or ionic bonding, or they may involve weaker interactions usually called **intermolecular forces** (because they occur between, rather than within, molecules).

*Although the densities of solid and liquid water are quite similar, as is typical for most substances, water is quite unusual in that the density of its solid state is slightly less than that of its liquid state. For most substances, the density of the solid state is slightly greater than that of the liquid state.

Intermolecular forces were introduced in Chapter 5 to explain nonideal gas behavior.

Remember that temperature is a measure of the random motions of the particles in a substance.

Dipole–dipole forces are forces that act between polar molecules.

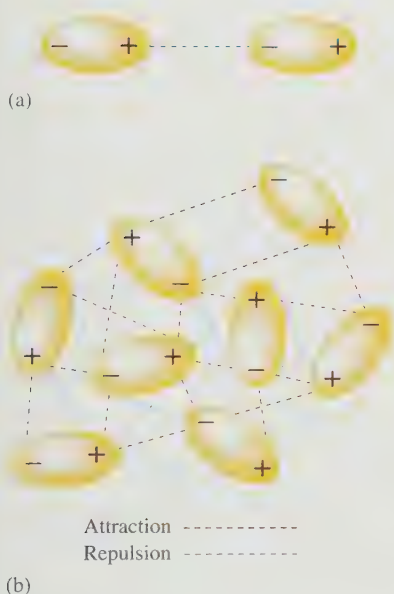


FIGURE 10.2

(a) The electrostatic interaction of two polar molecules. (b) The interaction of many dipoles in a condensed state.

FIGURE 10.3

(a) The polar water molecule. (b) Hydrogen bonding among water molecules. Note that the small size of the hydrogen atom allows for close interactions.

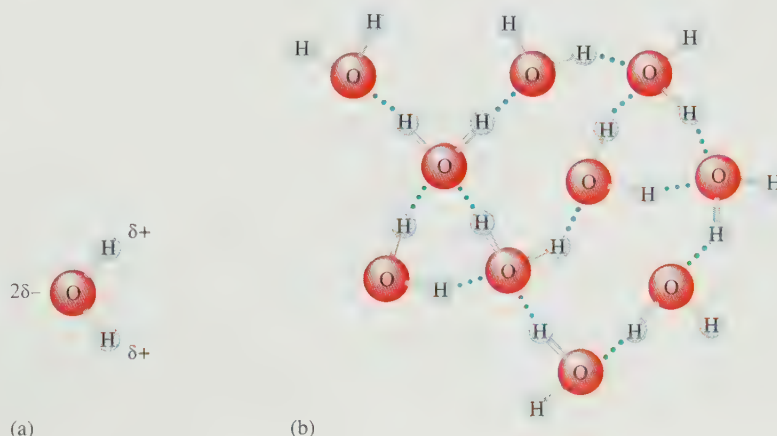
It is important to recognize that when a substance such as water changes from solid to liquid to gas, *the molecules remain intact*. The changes in states are due to changes in the forces *among* the molecules rather than in those *within* the molecules. In ice, as we will see later in this chapter, the molecules are virtually locked in place, although they can vibrate about their positions. If energy is added, the motions of the molecules increase, and they eventually achieve the greater movement and disorder characteristic of liquid water. The ice has melted. As more energy is added, the gaseous state is eventually reached, with the individual molecules far apart and interacting relatively little. However, the gas still consists of water molecules. It would take much energy to overcome the covalent bonds and decompose the water molecules into their component atoms. This can be seen by comparing the energy needed to vaporize 1 mole of liquid water (40.7 kJ) with that needed to break the O—H bonds in 1 mole of water molecules (934 kJ).

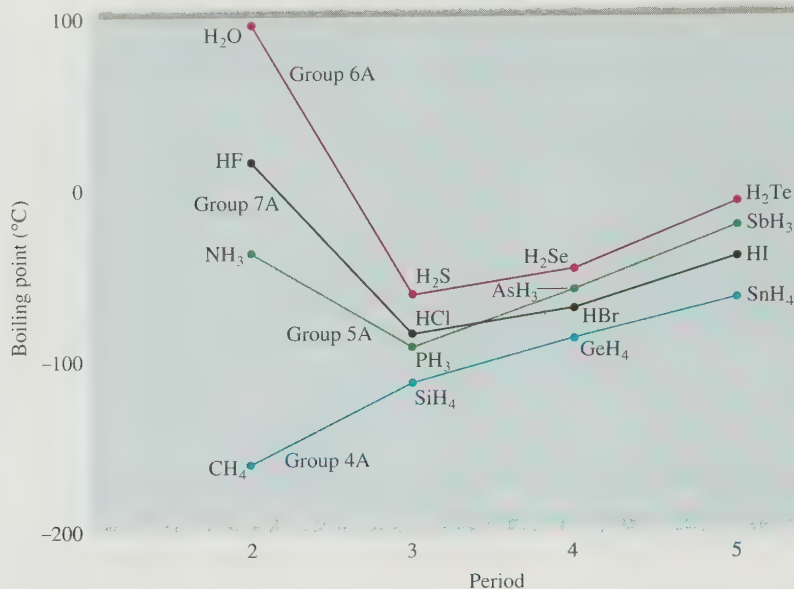
Dipole–Dipole Forces

As we saw in Section 8.3, molecules with polar bonds often behave in an electric field as if they had a center of positive charge and a center of negative charge. That is, they exhibit a dipole moment. Molecules with dipole moments can attract each other electrostatically by lining up so that the positive and negative ends are close to each other, as shown in Fig. 10.2(a). This is called a **dipole–dipole attraction**. In a condensed state such as a liquid, where many molecules are in close proximity, the dipoles find the best compromise between attraction and repulsion. That is, the molecules orient themselves to maximize the $\oplus\text{---}\ominus$ interactions and to minimize $\oplus\text{---}\oplus$ and $\ominus\text{---}\ominus$ interactions, as represented in Fig. 10.2(b).

Dipole–dipole forces are typically only about 1% as strong as covalent or ionic bonds, and they rapidly become weaker as the distance between the dipoles increases. At low pressures in the gas phase, where the molecules are far apart, these forces are relatively unimportant.

Particularly strong dipole–dipole forces, however, are seen among molecules in which hydrogen is bound to a highly electronegative atom, such as nitrogen, oxygen, or fluorine. Two factors account for the strengths of these interactions: the great polarity of the bond and the close approach of the dipoles, allowed by the very small size of the hydrogen atom. Because dipole–dipole attractions of this type are so unusually strong, they are given a special name—**hydrogen bonding**. Figure 10.3



**FIGURE 10.4**

The boiling points of the covalent hydrides of the elements in Groups 4A, 5A, 6A, and 7A.

shows hydrogen bonding among water molecules, which occurs between the partially positive H atoms and the lone pairs on adjacent water molecules.

Hydrogen bonding has a very important effect on physical properties. For example, the boiling points for the covalent hydrides of the elements in Groups 4A, 5A, 6A, and 7A are given in Fig. 10.4. Note that the nonpolar tetrahedral hydrides of Group 4A show a steady increase in boiling point with molar mass (that is, in going down the group), whereas, for the other groups, the lightest member has an unexpectedly high boiling point. Why? The answer lies in the especially large hydrogen bonding interactions that exist among the smallest molecules with the most polar X—H bonds. These unusually strong hydrogen bonding forces are due primarily to two factors. One factor is the relatively large electronegativity values of the lightest elements in each group, which leads to especially polar X—H bonds. The second factor is the small size of the first element of each group, which allows for the close approach of the dipoles, further strengthening the intermolecular forces. Because the interactions among the molecules containing the lightest elements in Groups 5A and 6A are so strong, an unusually large quantity of energy must be supplied to overcome these interactions and separate the molecules to produce the gaseous state. These molecules will remain together in the liquid state even at high temperatures—hence the very high boiling points.

Boiling point will be defined precisely in Section 10.8.

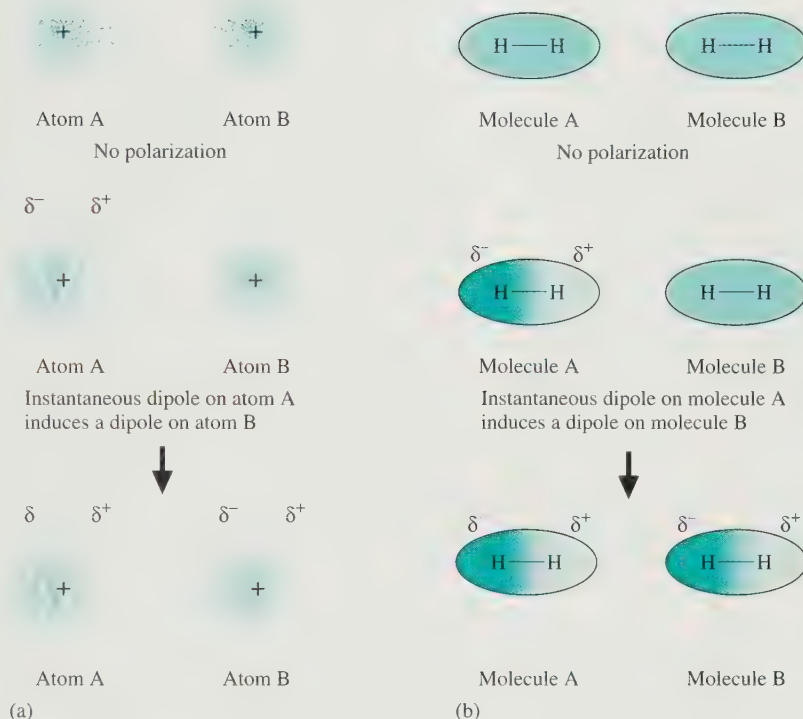
London Dispersion Forces

Even molecules without dipole moments must exert forces on each other. We know this because all substances—even the noble gases—exist in the liquid and solid states under certain conditions. The forces that exist among noble gas atoms and nonpolar molecules are called **London dispersion forces**. To understand the origin of these forces, let's consider a pair of noble gas atoms. Although we usually assume that the electrons of an atom are uniformly distributed about the nucleus, this is apparently not true at every instant. As the electrons move about the nucleus, a momentary nonsymmetrical electron distribution can develop that produces a temporary dipolar arrangement of charge. The formation of this temporary dipole can,

TABLE 10.2 The Freezing Points of the Group 8A Elements

Element	Freezing Point (°C)
Helium*	-269.7
Neon	-248.6
Argon	-189.4
Krypton	-157.3
Xenon	-111.9

*Helium is the only element that will not freeze by lowering its temperature at 1 atm. Pressure must be applied to freeze helium.

**FIGURE 10.5**

(a) An instantaneous polarization can occur on atom A, creating an instantaneous dipole. This dipole creates an induced dipole on neighboring atom B. (b) Nonpolar molecules such as H_2 also can develop instantaneous and induced dipoles.

in turn, affect the electron distribution of a neighboring atom. That is, this *instantaneous dipole* that occurs accidentally in a given atom can then *induce* a similar dipole in a neighboring atom, as represented in Fig. 10.5(a). This phenomenon leads to an interatomic attraction that is relatively weak and short-lived but that can be very significant especially for large atoms (see below). For these interactions to become strong enough to produce a solid, the motions of the atoms must be greatly slowed down. This explains, for instance, why the noble gas elements have such low freezing points (see Table 10.2).

Note from Table 10.2 that the freezing point rises going down the group. The principal cause for this trend is that as the atomic number increases, the number of electrons increases, and there is an increased chance of the occurrence of momentary dipole interactions. We describe this phenomenon using the term *polarizability*, which indicates the ease with which the electron “cloud” of an atom can be distorted to give a dipolar charge distribution. Thus we say that large atoms with many electrons exhibit a higher polarizability than small atoms. This means that the importance of London dispersion forces increases greatly as the size of the atom increases.

These same ideas also apply to nonpolar molecules such as H_2 , CH_4 , CCl_4 , and CO_2 [see Fig. 10.5(b)]. Since none of these molecules has a permanent dipole moment, their principal means of attracting each other is through London dispersion forces.

The dispersion forces in molecules with large atoms are quite significant and are often actually more important than dipole–dipole forces.

10.2 The Liquid State

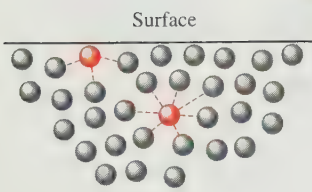


FIGURE 10.6
A molecule in the interior of a liquid is attracted by the molecules surrounding it, whereas a molecule at the surface of a liquid is attracted only by molecules below it and on each side.

For a given volume, a sphere has a smaller surface area than any other shape.

Surface tension: The resistance of a liquid to an increase in its surface area.

Liquids and liquid solutions are vital to our lives. Of course, water is the most important liquid. Besides being essential to life, water provides a medium for food preparation, for transportation, for cooling in many types of machines and industrial processes, for recreation, for cleaning, and for a myriad of other uses.

Liquids exhibit many characteristics that help us understand their nature. We have already mentioned their low compressibility, lack of rigidity, and high density compared with gases. Many of the properties of liquids give us direct information about the forces that exist among the particles. For example, when a liquid is poured onto a solid surface, it tends to bead as droplets, a phenomenon that depends on the intermolecular forces. Although molecules in the interior of the liquid are completely surrounded by other molecules, those at the liquid surface are subject to attractions only from the side and from below (Fig. 10.6). The effect of this uneven pull on the surface molecules tends to draw them into the body of the liquid and causes a droplet of liquid to assume the shape that has the minimum surface area—a sphere.

To increase a liquid's surface area, molecules must move from the interior of the liquid to the surface. This requires energy, since some intermolecular forces must be overcome. The resistance of a liquid to an increase in its surface area is called the **surface tension** of the liquid. As we would expect, liquids with relatively large intermolecular forces, such as those with polar molecules, tend to have relatively high surface tensions.

Polar liquids typically exhibit **capillary action**, the spontaneous rising of a liquid in a narrow tube. Two different types of forces are responsible for this property: *cohesive forces*, the intermolecular forces among the molecules of the liquid, and *adhesive forces*, the forces between the liquid molecules and their container. We have already seen how cohesive forces operate among polar molecules. Adhesive



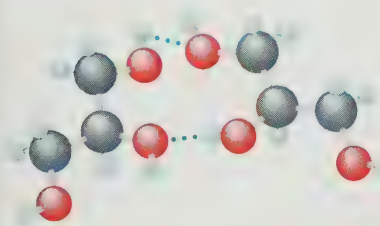
FIGURE 10.7
Nonpolar liquid mercury forms a convex meniscus in a glass tube, whereas polar water forms a concave meniscus.



Beads of water on a waxed car finish. The nonpolar component of the wax cause the water to form approximately spherical droplets.

The composition of glass is discussed in Section 10.5.

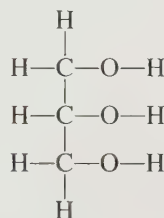
Viscosity: A measure of a liquid's resistance to flow.



Glycerol.

forces occur when a container is made of a substance that has polar bonds. For example, a glass surface contains many oxygen atoms with partial negative charges that are attractive to the positive end of a polar molecule such as water. This ability of water to “wet” glass makes it creep up the walls of the tube where the water surface touches the glass. This, however, tends to increase the surface area of the water, which is opposed by the cohesive forces that try to minimize the surface. Thus, because water has both strong cohesive (intermolecular) forces and strong adhesive forces to glass, it “pulls itself” up a glass capillary tube (a tube with a small diameter) to a height where the weight of the column of water just balances the water’s tendency to be attracted to the glass surface. The concave shape of the meniscus (see Fig. 10.7) shows that water’s adhesive forces toward the glass are stronger than its cohesive forces. A nonpolar liquid such as mercury (see Fig. 10.7) shows a convex meniscus. This behavior is characteristic of a liquid in which the cohesive forces are stronger than the adhesive forces toward glass.

Another property of liquids strongly dependent on intermolecular forces is **viscosity**, a measure of a liquid’s resistance to flow. As might be expected, liquids with large intermolecular forces tend to be highly viscous. For example, glycerol, whose structure is



has an unusually high viscosity due mainly to its high capacity to form hydrogen bonds using its O—H groups (see margin).

Molecular complexity also leads to higher viscosity because very large molecules can become entangled with each other. For example, gasoline, a nonviscous liquid, contains hydrocarbon molecules of the type $\text{CH}_3-(\text{CH}_2)_n-\text{CH}_3$, where n varies from about 3 to 8. However, grease, which is very viscous, contains much larger hydrocarbon molecules in which n varies from 20 to 25.

Structural Model for Liquids

In many respects, the development of a structural model for liquids presents greater challenges than the development of such a model for the other two states of matter. In the gaseous state the particles are so far apart and are moving so rapidly that intermolecular forces are negligible under most circumstances. This means that we can use a relatively simple model for gases. In the solid state, although the intermolecular forces are large, the molecular motions are minimal, and fairly simple models are again possible. The liquid state, however, has both strong intermolecular forces *and* significant molecular motions. Such a situation precludes the use of really simple models for liquids. Recent advances in *spectroscopy*, the study of the manner in which substances interact with electromagnetic radiation, make it possible to follow the very rapid changes that occur in liquids. As a result, our models of liquids are becoming more accurate. As a starting point, a typical liquid might best be viewed as containing a large number of regions where the arrangements of the components are similar to those found in the solid, but with more disorder, and

a smaller number of regions where holes are present. The situation is highly dynamic, with rapid fluctuations occurring in both types of regions.

10.3 *An Introduction to Structures and Types of Solids*

There are many ways to classify solids, but the broadest categories are **crystalline solids**, those with a highly regular arrangement of their components, and **amorphous solids**, those with considerable disorder in their structures.

The regular arrangement of the components of a crystalline solid at the microscopic level produces the beautiful, characteristic shapes of crystals, such as those shown in Fig. 10.8. The positions of the components in a crystalline solid are usually represented by a **lattice**, a three-dimensional system of points designating the positions of the components (atoms, ions, or molecules) that make up the substance. The *smallest repeating unit* of the lattice is called the **unit cell**. Thus a particular lattice can be generated by repeating the unit cell in all three dimensions to form the extended structure. Three common unit cells and their lattices are shown in Fig. 10.9. Note from Fig. 10.9 that the extended structure in each case can be viewed as a series of repeating unit cells that share common faces in the interior of the solid.

Although we will concentrate on crystalline solids in this book, there are many important noncrystalline (amorphous) materials. An example is common glass, which is best pictured as a solution in which the components are “frozen in place” before they can achieve an ordered arrangement. Although glass is a solid (it has a rigid shape), a great deal of disorder exists in its structure.

X-Ray Analysis of Solids

The structures of crystalline solids are most commonly determined by **X-ray diffraction**. Diffraction occurs when beams of light are scattered from a regular array of points in which the spacings between the components are comparable with the



FIGURE 10.8
Two crystalline solids: pyrite (left), amethyst (right).

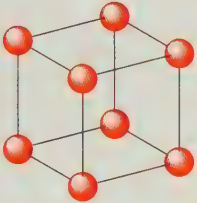
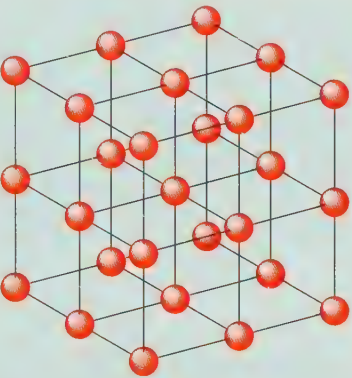
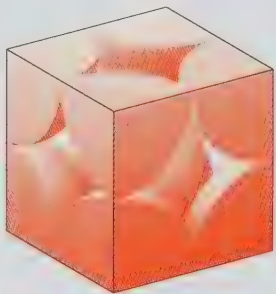
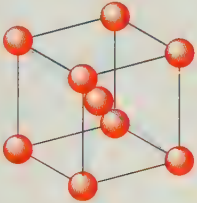
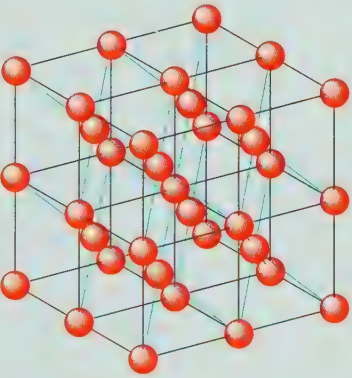
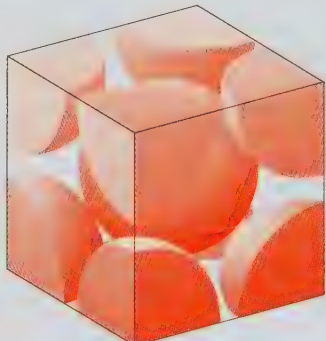
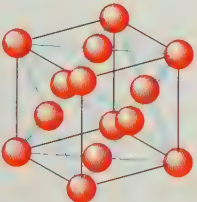
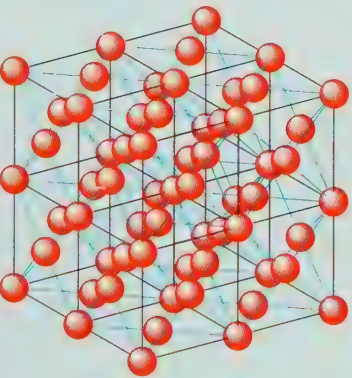
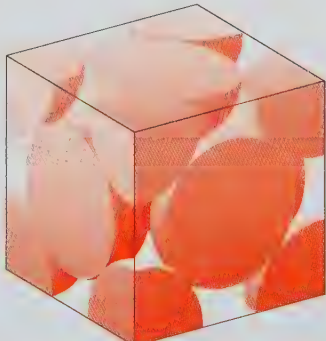
	Unit cell	Lattice	Space-filling unit cell	Example
(a)	 Simple cubic			Polonium metal
(b)	 Body-centered cubic			Uranium metal
(c)	 Face-centered cubic			Gold metal

FIGURE 10.9

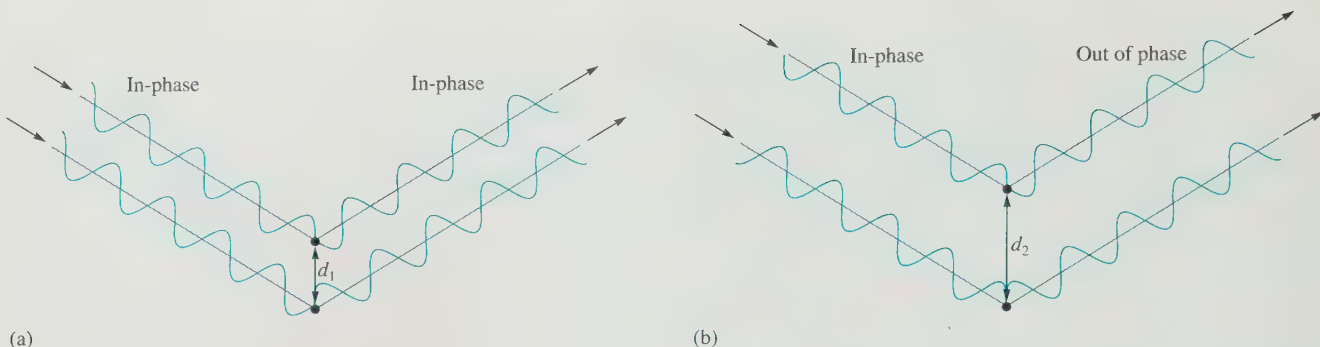
Three cubic unit cells and the corresponding lattices. Note that only parts of spheres on the corners and faces of the unit cells reside inside the unit cell, as shown by the “cut-off” versions.



Visualization: Unit Cells and Crystal Packing

wavelength of the light. Diffraction is due to constructive interference when the waves of parallel beams are in phase and to destructive interference when the waves are out of phase.

When X rays of a single wavelength are directed at a crystal, a diffraction pattern is obtained, as we saw in Fig. 7.5. The light and dark areas on the photographic

**FIGURE 10.10**

X rays scattered from two different atoms may reinforce (constructive interference) or cancel (destructive interference) one another. (a) Both the incident rays and the reflected rays are also in phase. In this case, d_1 is such that the difference in the distances traveled by the two rays is a whole number of wavelengths. (b) The incident rays are in phase but the reflected rays are exactly out of phase. In this case d_2 is such that the difference in distances traveled by the two rays is an odd number of half wavelengths.

plate occur because the waves scattered from various atoms may reinforce or cancel each other (see Fig. 10.10). The key to whether the waves reinforce or cancel is the difference in distance traveled by the waves after they strike the atoms. The waves are in phase before they are reflected, so if the difference in distance traveled is an *integral number of wavelengths*, the waves will still be in phase.

Since the distance traveled depends on the distance between the atoms, the diffraction pattern can be used to determine the interatomic spacings. The exact relationship can be worked out using the diagram in Fig. 10.11, which shows two in-phase waves being reflected by atoms in two different layers in a crystal. The extra distance traveled by the lower wave is the sum of the distances xy and yz , and the waves will be in phase after reflection if

$$xy + yz = n\lambda \quad (10.1)$$

where n is an integer and λ is the wavelength of the X rays. Using trigonometry (see Fig. 10.11), we can show that

$$xy + yz = 2d \sin \theta \quad (10.2)$$

where d is the distance between the atoms and θ is the angle of incidence and reflection. Combining Equation (10.1) and Equation (10.2) gives

$$n\lambda = 2d \sin \theta \quad (10.3)$$

Equation (10.3) is called the *Bragg equation* after William Henry Bragg (1862–1942) and his son William Lawrence Bragg (1890–1972), who shared the Nobel Prize in physics in 1915 for their pioneering work in X-ray crystallography.

A diffractometer is a computer-controlled instrument used for carrying out the X-ray analysis of crystals. It rotates the crystal with respect to the X-ray beam and collects the data produced by the scattering of the X rays from the various planes of atoms in the crystal. The results are then analyzed by computer.

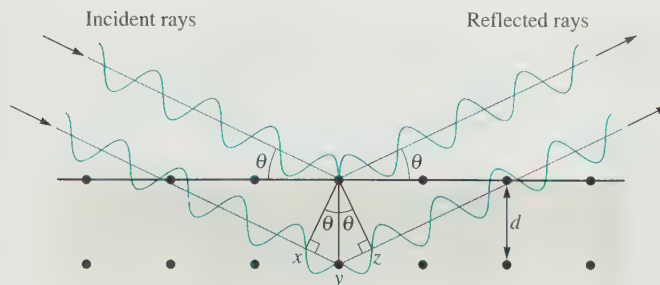
The techniques for crystal structure analysis have reached a level of sophistication that allows the determination of very complex structures, such as those important in biological systems. For example, the structures of several enzymes have been determined, thus enabling biochemists to understand how they perform their functions. We will explore this topic further in Chapter 12. Using X-ray diffraction, we can gather data on bond lengths and angles and in so doing can test the predictions of our models of molecular geometry.



Graduate student Maria Zhuravlera operating an X-ray diffractometer at Michigan State University.

FIGURE 10.11

Reflection of X rays of wavelength λ from a pair of atoms in two different layers of a crystal. The lower wave travels an extra distance equal to the sum of xy and yz . If this distance is an integral number of wavelengths ($n = 1, 2, 3, \dots$), the waves will reinforce each other when they exit the crystal.



SAMPLE EXERCISE 10.1

Using the Bragg Equation

X rays of wavelength $1.54 \text{ \AA}$ were used to analyze an aluminum crystal. A reflection was produced at $\theta = 19.3$ degrees. Assuming $n = 1$, calculate the distance d between the planes of atoms producing this reflection.

SOLUTION

To determine the distance between the planes, we use Equation (10.3) with $n = 1$, $\lambda = 1.54 \text{ \AA}$, and $\theta = 19.3$ degrees. Since $2d \sin \theta = n\lambda$,

$$d = \frac{n\lambda}{2 \sin \theta} = \frac{(1)(1.54 \text{ \AA})}{(2)(0.3305)} = 2.33 \text{ \AA} = 233 \text{ pm}$$

See Exercises 10.45 and 10.46.

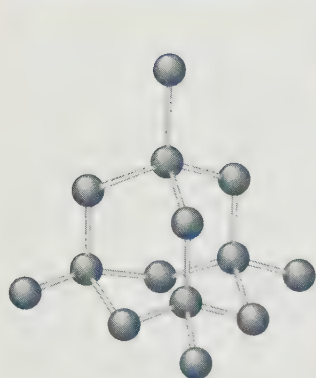
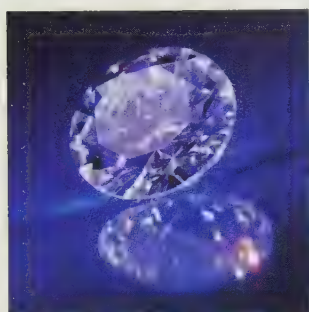
Types of Crystalline Solids

There are many different types of crystalline solids. For example, although both sugar and salt dissolve readily in water, the properties of the resulting solutions are quite different. The salt solution readily conducts an electric current, whereas the sugar solution does not. This behavior arises from the nature of the components in these two solids. Common salt (NaCl) is an ionic solid; it contains Na^+ and Cl^- ions. When solid sodium chloride dissolves in the polar water, sodium and chloride ions are distributed throughout the resulting solution and are free to conduct electric current. Table sugar (sucrose), on the other hand, is composed of neutral molecules that are dispersed throughout the water when the solid dissolves. No ions are present, and the resulting solution does not conduct electricity. These examples illustrate two important types of solids: **ionic solids**, represented by sodium chloride, and **molecular solids**, represented by sucrose. Ionic solids have ions at the points of the lattice that describes the structure of the solid. A molecular solid, on the other hand, has discrete covalently bonded molecules at each of its lattice points. Ice is a molecular solid that has an H_2O molecule at each point (see Fig. 10.12).

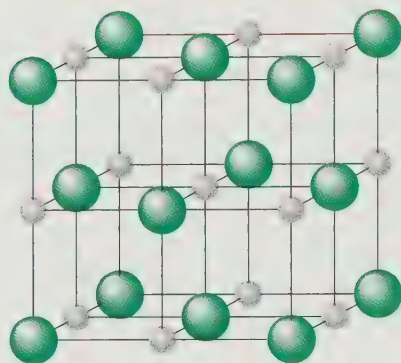
A third type of solid is represented by elements such as carbon (which exists in the forms graphite, diamond, and the fullerenes), boron, silicon, and all metals. These substances all have atoms at the lattice points that describe the structure of the solid. Therefore, we call solids of this type **atomic solids**. Examples of these three types of solids are shown in Fig. 10.12.

To summarize, we find it convenient to classify solids according to what type of component occupies the lattice points. This leads to the classifications *atomic*

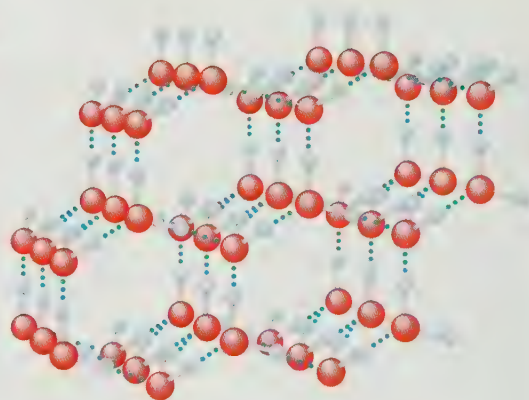
Buckminsterfullerene, C_{60} , is a particular member of the fullerene family.



● C
Diamond
(a)



● Cl⁻
● Na⁺
Sodium chloride
(b)



● H₂O
Ice
(c)

FIGURE 10.12

Examples of three types of crystalline solids. Only part of the structure is shown in each case. (a) An atomic solid. (b) An ionic solid. (c) A molecular solid. The dotted lines show the hydrogen bonding interactions among the polar water molecules.

solids (atoms at the lattice points), *molecular solids* (discrete, relatively small molecules at the lattice points), and *ionic solids* (ions at the lattice points). In addition, atomic solids are placed into the following subgroups based on the bonding that exists among the atoms in the solid: *metallic solids*, *network solids*, and *Group 8A solids*. In metallic solids, a special type of delocalized nondirectional covalent bonding occurs. In network solids, the atoms bond to each other with strong directional covalent bonds that lead to giant molecules, or networks, of atoms. In the Group 8A solids, the noble gas elements are attracted to each other with London dispersion forces. The classification of solids is summarized in Table 10.3.

The markedly different bonding present in the various atomic solids leads to dramatically different properties for the resulting solids. For example, although argon, copper, and diamond all are atomic solids, they have strikingly different properties. Argon (a Group 8A solid) has a very low melting point (-189°C), whereas diamond (a network solid) and copper (a metallic solid) melt at high temperatures (about 3500 and 1083°C , respectively). Copper is an excellent conductor of electricity, whereas argon and diamond are both insulators. Copper can be easily changed in shape; it is both malleable (can be formed into thin sheets) and ductile (can be pulled into a wire). Diamond, on the other hand, is the hardest natural substance known. We will explore the structure and bonding of atomic solids in the next two sections.

The internal forces in a solid determine the properties of the solid.

TABLE 10.3 Classification of Solids

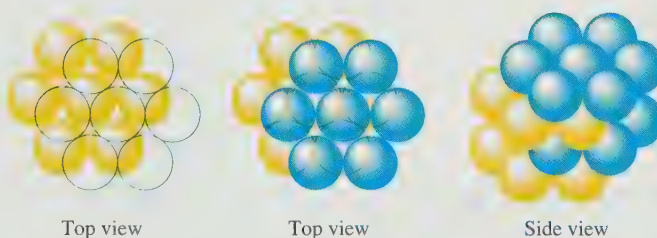
	Atomic Solids			Molecular Solids	Ionic Solids
	Metallic	Network	Group 8A		
Components That Occupy the Lattice Points:	Metal atoms	Nonmetal atoms	Group 8A atoms	Discrete molecules	Ions
Bonding:	Delocalized covalent	Directional covalent (leading to giant molecules)	London dispersion forces	Dipole–dipole and/or London dispersion forces	Ionic

10.4 Structure and Bonding in Metals

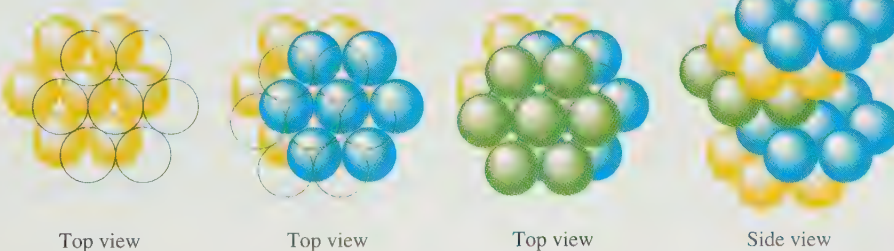
Metals are characterized by high thermal and electrical conductivity, malleability, and ductility. As we will see, these properties can be traced to the nondirectional covalent bonding found in metallic crystals.

A metallic crystal can be pictured as containing spherical atoms packed together and bonded to each other equally in all directions. We can model such a structure by packing uniform, hard spheres in a manner that most efficiently uses the available space. Such an arrangement is called **closest packing**. The spheres are packed in layers, as shown in Fig. 10.13, in which each sphere is surrounded by six others. In the second layer the spheres do not lie directly over those in the first layer. Instead, each one occupies an indentation (or dimple) formed by three spheres in the first layer. In the third layer the spheres can occupy the dimples of the second layer in two possible ways: They can occupy positions so that each sphere in the third layer lies directly over a sphere in the first layer (the *aba* arrangement; Fig. 10.13a), or they can occupy positions so that no sphere in the third layer lies over one in the first layer (the *abc* arrangement; Fig. 10.13b).

(a) *abab* — Closest packing



(b) *abca* — Closest packing

**FIGURE 10.13**

The closest packing arrangement of uniform spheres. In each layer a given sphere is surrounded by six others, creating six dimples, only three of which can be occupied in the next layer. (a) *aba* packing: The second layer is like the first, but it is displaced so that each sphere in the second layer occupies a dimple in the first layer. The spheres in the third layer occupy dimples in the second layer so that the spheres in the third layer lie directly over those in the first layer (*aba*). (b) *abc* packing: The spheres in the third layer occupy dimples in the second layer so that no spheres in the third layer lie above any in the first layer (*abc*). The fourth layer is like the first.

The closest packing model for metallic crystals assumes that metal atoms are uniform, hard spheres.

CHEMICAL IMPACT

Seething Surfaces

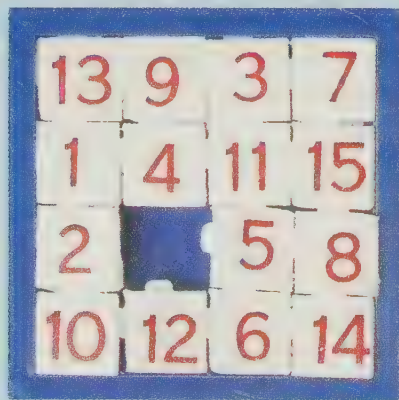
When we picture a solid, we think of the particles as being packed closely together with relatively little motion. The particles are thought to vibrate randomly about their positions but stay in nearly the same place. Recent research, however, indicates surface particles are a great deal more mobile than was previously thought. Independent teams of scientists from the University of Leiden in the Netherlands and Sandia National Laboratory in New Mexico have found a surprising amount of atom-swapping occurring on the surface of a copper crystal.

The Dutch scientist Raoul van Gastel and his colleagues used a scanning tunneling microscope (STM) to study the surface of a copper crystal containing indium atom impurities. They noted that a given patch of surface would stay the same for several scans and then, suddenly, the indium atoms would appear at different places. Surprisingly, the indium atoms seemed to make “long jumps,” moving as many as five atom positions between scans. The most likely explanation for these movements is a “hole” created by a copper atom escaping the surface. This hole moves around as other atoms shift to fill it in succession (see accompanying figure). The best analogy to the movement of the hole is the toy slide puzzle with 15 numbered pieces and one missing

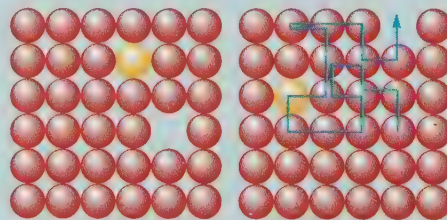
piece in a 4×4 array. The object of the game is to slide a piece into the hole and then repeat the process until the numbers appear in order.

The hole on the copper surface moves very fast—up to 100 million times per second—shuffling copper atoms and allowing the indium atoms to change positions. Van Gastel believes that all of the observed motion results from just a few fast-moving holes. In fact, he suggests that just one in 6 billion copper atoms is missing at a given time, analogous to one person in the entire earth’s population. Its absence causes a given atom on the surface to move every 30 or 40 seconds. Brian Swartzentruber of Sandia National Laboratories came to similar conclusions using an STM to track the movement of palladium atoms on a copper surface.

These results have important implications. For example, metal surfaces are often used to speed up particular reactions. The motions on the metal surface could significantly influence the way that reactants interact with the surface. Also, a lot of effort is now being expended to construct tiny “machines” (called nanoscale devices) by assembling individual atoms on a solid surface. These devices could be literally torn apart by excess surface motions.



A toy slide puzzle.



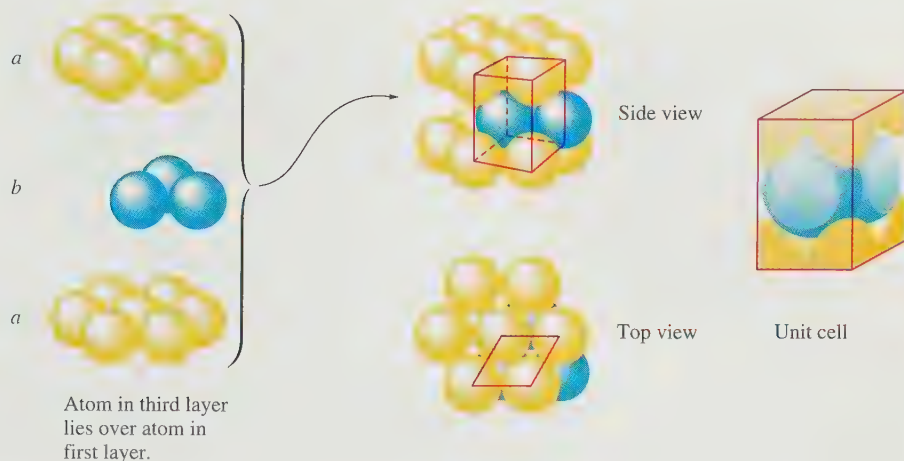
A section of a surface containing copper atoms (red) and an indium atom (yellow). A hole due to a missing copper atom is shown on the left. The blue line on the right shows the movement of this hole. As an atom moves to fill the hole, the hole moves as well. In the process, the indium atom jumps to a new position.

Illustration from van Gastel, et al., *Physical Review Letters*, Feb. 19, 2001, Vol. 86, Issue 5, pp. 1562–1565. Copyright 2001 by the American Physical Society.

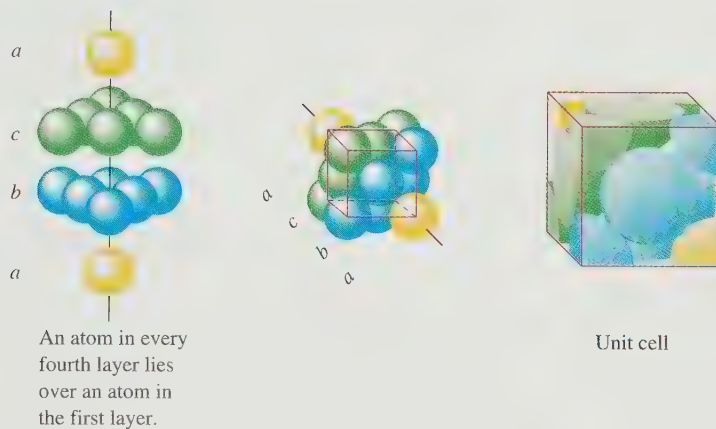
The *aba* arrangement has the *hexagonal* unit cell shown in Fig. 10.14, and the resulting structure is called the **hexagonal closest packed (hcp) structure**. The *abc* arrangement has a *face-centered cubic* unit cell, as shown in Fig. 10.15, and the resulting structure is called the **cubic closest packed (ccp) structure**. Note

FIGURE 10.14

When spheres are closest packed so that the spheres in the third layer are directly over those in the first layer (*aba*), the unit cell is the hexagonal prism illustrated here in red.

**FIGURE 10.15**

When spheres are packed in the *abc* arrangement, the unit cell is face-centered cubic. To make the cubic arrangement easier to see, the vertical axis has been tilted as shown.



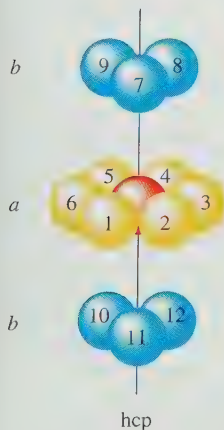
that in the hcp structure the spheres in every other layer occupy the same vertical position (*ababab* . . .), whereas in the ccp structure the spheres in every fourth layer occupy the same vertical position (*abcabca* . . .). A characteristic of both structures is that each sphere has 12 equivalent nearest neighbors: 6 in the same layer, 3 in the layer above, and 3 in the layer below (that form the dimples). This is illustrated for the hcp structure in Fig. 10.16.

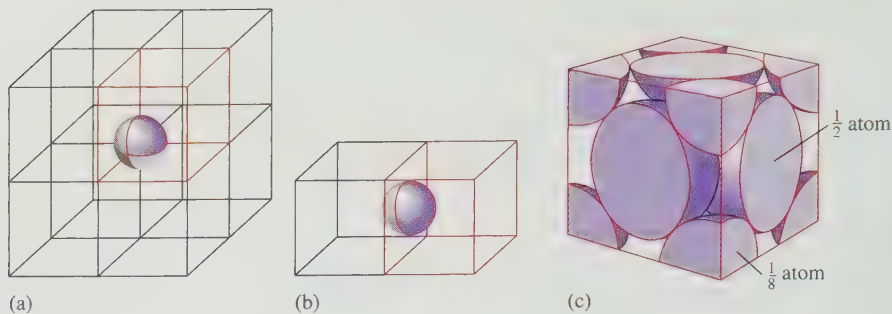
Knowing the *net* number of spheres (atoms) in a particular unit cell is important for many applications involving solids. To illustrate how to find the net number of spheres in a unit cell, we will consider a face-centered cubic unit cell (Fig. 10.17). Note that this unit cell is defined by the *centers* of the spheres on the cube's corners. Thus 8 cubes share a given sphere, so $\frac{1}{8}$ of this sphere lies inside each unit cell. Since a cube has 8 corners, there are $8 \times \frac{1}{8}$ pieces, or enough to put together 1 whole sphere. The spheres at the center of each face are shared by 2 unit cells, so $\frac{1}{2}$ of each lies inside a particular unit cell. Since the cube has 6 faces, we have $6 \times \frac{1}{2}$ pieces, or enough to construct 3 whole spheres. Thus the net number of spheres in a face-centered cubic unit cell is

$$\left(8 \times \frac{1}{8}\right) + \left(6 \times \frac{1}{2}\right) = 4$$

FIGURE 10.16

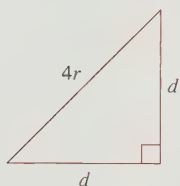
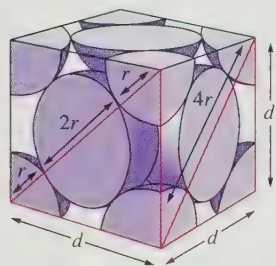
The indicated sphere has 12 nearest neighbors.



**FIGURE 10.17**

The net number of spheres in a face-centered cubic unit cell. (a) Note that the sphere on a corner of the colored cell is shared with 7 other unit cells (a total of 8). Thus $\frac{1}{8}$ of such a sphere lies within a given unit cell. Since there are 8 corners in a cube, there are 8 of these $\frac{1}{8}$ pieces, or 1 net sphere. (b) The sphere on the center of each face is shared by 2 unit cells, and thus each unit cell has $\frac{1}{2}$ of each of these types of spheres. There are 6 of these $\frac{1}{2}$ spheres to give 3 net spheres. (c) Thus the face-centered cubic unit cell contains 4 net spheres (all of the pieces can be assembled to give 4 spheres).

SAMPLE EXERCISE 10.2



Calculating the Density of a Closest Packed Solid

Silver crystallizes in a cubic closest packed structure. The radius of a silver atom is 144 pm. Calculate the density of solid silver.

SOLUTION

Density is mass per unit volume. Thus we need to know how many silver atoms occupy a given volume in the crystal. The structure is cubic closest packed, which means the unit cell is face-centered cubic, as shown in the accompanying figure.

We must find the volume of this unit cell for silver and the net number of atoms it contains. Note that in this structure the atoms touch along the diagonals for each face and not along the edges of the cube. Thus the length of the diagonal is $r + 2r + r$, or $4r$. We use this fact to find the length of the edge of the cube by the Pythagorean theorem:

$$\begin{aligned} d^2 + d^2 &= (4r)^2 \\ 2d^2 &= 16r^2 \\ d^2 &= 8r^2 \\ d &= \sqrt{8r^2} = r\sqrt{8} \end{aligned}$$

Since $r = 144$ pm for a silver atom,

$$d = (144 \text{ pm})(\sqrt{8}) = 407 \text{ pm}$$

The volume of the unit cell is d^3 , which is $(407 \text{ pm})^3$, or $6.74 \times 10^7 \text{ pm}^3$. We convert this to cubic centimeters as follows:

$$6.74 \times 10^7 \text{ pm}^3 \times \left(\frac{1.00 \times 10^{-10} \text{ cm}}{\text{pm}} \right)^3 = 6.74 \times 10^{-23} \text{ cm}^3$$

Since we know that the net number of atoms in the face-centered cubic unit cell is 4, we have 4 silver atoms contained in a volume of $6.74 \times 10^{-23} \text{ cm}^3$. The density is therefore

$$\begin{aligned} \text{Density} &= \frac{\text{mass}}{\text{volume}} = \frac{(4 \text{ atoms})(107.9 \text{ g/mol})(1 \text{ mol}/6.022 \times 10^{23} \text{ atoms})}{6.74 \times 10^{-23} \text{ cm}^3} \\ &= 10.6 \text{ g/cm}^3 \end{aligned}$$

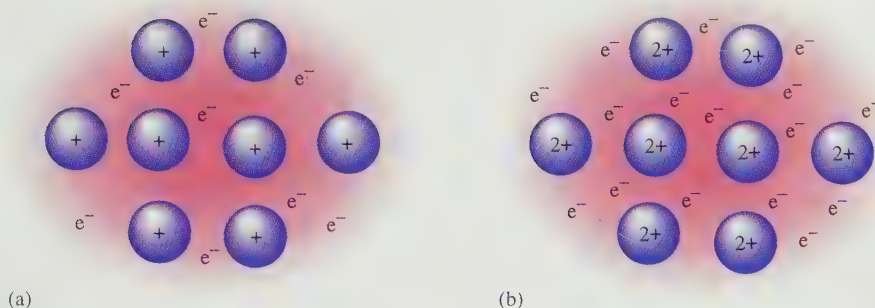


Crystalline silver contains cubic closest packed silver atoms.

See Exercises 10.47 through 10.50.

FIGURE 10.18

The electron sea model for metals postulates a regular array of cations in a “sea” of valence electrons. (a) Representation of an alkali metal (Group 1A) with one valence electron. (b) Representation of an alkaline earth metal (Group 2A) with two valence electrons.



Examples of metals that form cubic closest packed solids are aluminum, iron, copper, cobalt, and nickel. Magnesium and zinc are hexagonal closest packed. Calcium and certain other metals can crystallize in either of these structures. Some metals, however, assume structures that are not closest packed. For example, the alkali metals have structures characterized by a *body-centered cubic (bcc) unit cell* (see Fig. 10.9), where the spheres touch along the body diagonal of the cube. In this structure, each sphere has 8 nearest neighbors (count the number of atoms around the atom at the center of the unit cell), as compared with 12 in the closest packed structures. Why a particular metal adopts the structure it does is not well understood.

Malleable: Can be pounded into thin sheets.

Ductile: Can be drawn to form a wire.

Bonding Models for Metals

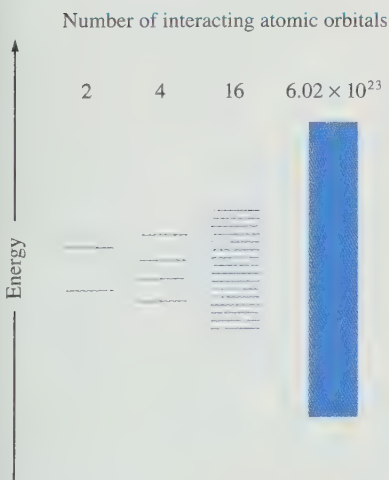
Any successful bonding model for metals must account for the typical physical properties of metals: malleability, ductility, and the efficient and uniform conduction of heat and electricity in all directions. Although the shapes of most pure metals can be changed relatively easily, most metals are durable and have high melting points. These facts indicate that the bonding in most metals is both *strong* and *nondirectional*. That is, although it is difficult to separate metal atoms, it is relatively easy to move them, provided the atoms stay in contact with each other.

The simplest picture that explains these observations is the *electron sea model*, which envisions a regular array of metal cations in a “sea” of valence electrons (see Fig. 10.18). The mobile electrons can conduct heat and electricity, and the metal ions can be easily moved around as the metal is hammered into a sheet or pulled into a wire.

A related model that gives a more detailed view of the electron energies and motions is the **band model**, or **molecular orbital (MO) model**, for metals. In this model, the electrons are assumed to travel around the metal crystal in molecular orbitals formed from the valence atomic orbitals of the metal atoms (Fig. 10.19).

Recall that in the MO model for the gaseous Li_2 molecule (Section 9.3), two widely spaced molecular orbital energy levels (bonding and antibonding) result when two identical atomic orbitals interact. However, when many metal atoms interact, as in a metal crystal, the large number of resulting molecular orbitals become more closely spaced and finally form a virtual continuum of levels, called *bands*, as shown in Fig. 10.19.

As an illustration, picture a magnesium metal crystal, which has an hcp structure. Since each magnesium atom has one $3s$ and three $3p$ valence atomic orbitals, a crystal with n magnesium atoms has available $n(3s)$ and $3n(3p)$ orbitals to form the molecular orbitals, as illustrated in Fig. 10.20. Note that the core electrons are localized, as shown by their presence in the energy “well” around each magnesium

**FIGURE 10.19**

The molecular orbital energy levels produced when various numbers of atomic orbitals interact. Note that for two atomic orbitals two rather widely spaced energy levels result. (Recall the description of H_2 in Section 9.2.) As more atomic orbitals are available to form molecular orbitals, the resulting energy levels are more closely spaced, finally producing a band of very closely spaced orbitals.

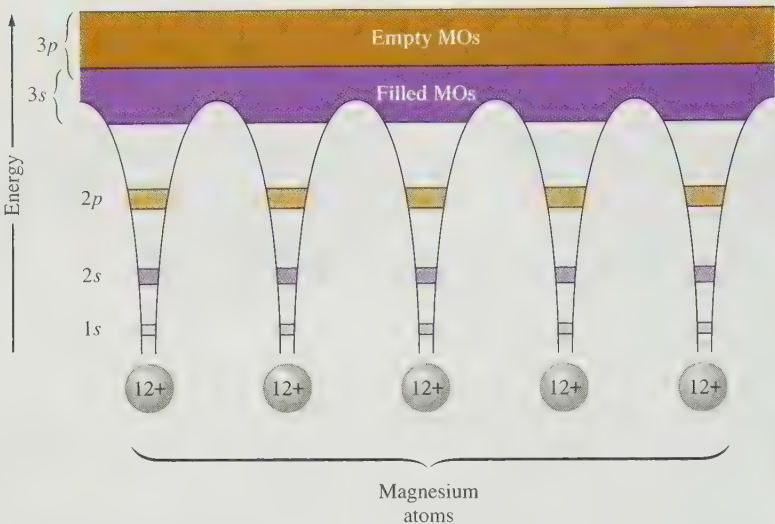
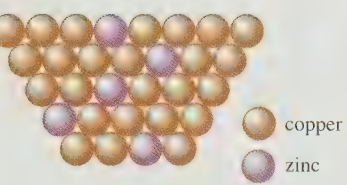


FIGURE 10.20
(above) A representation of the energy levels (bands) in a magnesium crystal. The electrons in the 1s, 2s, and 2p orbitals are close to the nuclei and thus are localized on each magnesium atom as shown. However, the 3s and 3p valence orbitals overlap and mix to form molecular orbitals. Electrons in these energy levels can travel throughout the crystal. (photo at right) Crystals of magnesium grown from a vapor.

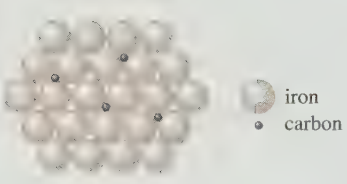
atom. However, the valence electrons occupy closely spaced molecular orbitals, which are only partially filled.

The existence of empty molecular orbitals close in energy to filled molecular orbitals explains the thermal and electrical conductivity of metal crystals. Metals conduct electricity and heat very efficiently because of the availability of highly mobile electrons. For example, when an electric potential is placed across a strip of metal, for current to flow, electrons must be free to move. In the band model for metals, mobile electrons are furnished when electrons in filled molecular orbitals are excited into empty ones. These conduction electrons are free to travel throughout the metal crystal as dictated by the potential imposed on the metal. The molecular orbitals occupied by these conducting electrons are called *conduction bands*. These mobile electrons also account for the efficiency of the conduction of heat through metals. When one end of a metal rod is heated, the mobile electrons can rapidly transmit the thermal energy to the other end.



Brass

(a)



Steel

(b)

FIGURE 10.21
Two types of alloys.

Metal Alloys

Because of the nature of the structure and bonding of metals, other elements can be introduced into a metallic crystal relatively easily to produce substances called alloys. An **alloy** is best defined as *a substance that contains a mixture of elements and has metallic properties*. Alloys can be conveniently classified into two types.

In a **substitutional alloy** some of the host metal atoms are *replaced* by other metal atoms of similar size. For example, in brass, approximately one-third of the atoms in the host copper metal have been replaced by zinc atoms, as shown in Fig. 10.21(a). Sterling silver (93% silver and 7% copper), pewter (85% tin, 7% copper, 6% bismuth, and 2% antimony), and plumber's solder (95% tin and 5% antimony) are other examples of substitutional alloys.

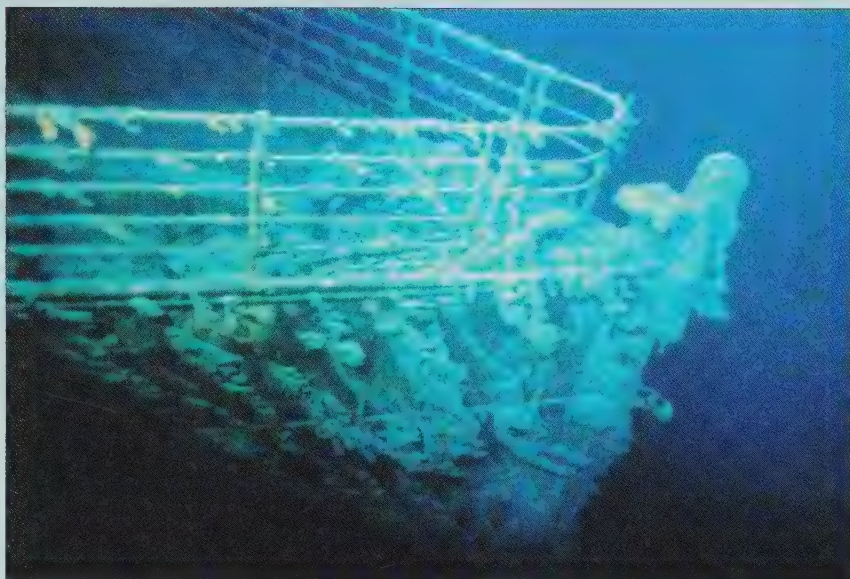
An **interstitial alloy** is formed when some of the interstices (holes) in the closest packed metal structure are occupied by small atoms, as shown in Fig. 10.21(b). Steel, the best known interstitial alloy, contains carbon atoms in the holes of an iron crystal. The presence of the interstitial atoms changes the properties of the host

CHEMICAL IMPACT

What Sank the Titanic?

On April 12, 1912, the steamship *Titanic* struck an iceberg in the North Atlantic approximately 100 miles south of the Grand Banks of Newfoundland and within 3 hours was resting on the bottom of the ocean. Of her more than 2300 passengers and crew, over 1500 lost their lives. While the tragic story of the *Titanic* has never faded from the minds and imaginations of the generations that followed, the 1985 discovery of the wreck by a joint Franco-American expedition at a depth of 12,612 feet rekindled the world's interest in the "greatest ocean-going vessel" ever built. The discovery also would reveal important scientific clues as to why and how the *Titanic* sank so quickly in the frigid waters of the North Atlantic.

The *Titanic* was designed to be virtually "unsinkable," and even in the worst case scenario, a head-on collision with another ocean liner, the ship was engineered to take from one to three days to sink. Thus its quick trip to the bottom has puzzled scientists for years. In 1991, Steve Blasco, an ocean-floor geologist for the Canadian Department of Natural Resources, led a scientific expedition to the wreck. On one of 17 dives to the site, Blasco's team recovered a piece of steel that appeared to be a part of the *Titanic*'s hull. Unlike modern steel, which would have shown evidence of bending in a collision, the steel recovered from the *Titanic* appeared to have shattered on impact with the iceberg. This suggested that the metal might not have been as ductile (*ductility* is the ability to stretch without breaking) as it should have been. In 1994, tests were conducted on small pieces of metal, called *coupons*, cut from the recovered piece of hull. These samples shattered without bending. Further analysis showed that the steel used to construct the hull of the *Titanic* was high in sulfur content, and it is known that sulfur occlusions tend to make steel more brittle. This evidence suggests that the



Bow of the *Titanic* under $2\frac{1}{2}$ miles of water.

quality of the steel used to make the hull of the *Titanic* may very well have been an important factor that led to the rapid sinking of the ship.

But—not so fast. The *Titanic* continues to provoke controversy. A team of naval engineers and scientists recently have concluded that it was not brittle steel but faulty rivets that doomed the *Titanic*. During expeditions in 1996 and 1998 conducted by RMS Titanic, Inc., more samples of *Titanic*'s steel and rivets were obtained for further study. Analysis of these samples by a team headed by Tim Foecke of the National Institute of Standards and Technology (NIST) shows that the rivets contain three times the expected amount of silicate slag. Foecke and his colleagues argue that the high slag content resulted in weak rivets that snapped in large numbers when the collision occurred, mortally wounding the ship.

What sank the *Titanic*? It hit an iceberg. The details remain to be figured out.

metal. Pure iron is relatively soft, ductile, and malleable due to the absence of directional bonding. The spherical metal atoms can be rather easily moved with respect to each other. However, when carbon, which forms strong directional bonds, is introduced into an iron crystal, the presence of the directional carbon-iron bonds

TABLE 10.4 The Composition of the Two Brands of Steel Tubing Commonly Used to Make Lightweight Racing Bicycles

Brand of Tubing	% C	% Si	% Mn	% Mo	% Cr
Reynolds	0.25	0.25	1.3	0.20	—
Columbus	0.25	0.30	0.65	0.20	1.0

makes the resulting alloy harder, stronger, and less ductile than pure iron. The amount of carbon directly affects the properties of steel. *Mild steels*, containing less than 0.2% carbon, are ductile and malleable and are used for nails, cables, and chains. *Medium steels*, containing 0.2 to 0.6% carbon, are harder than mild steels and are used in rails and structural steel beams. *High-carbon steels*, containing 0.6 to 1.5% carbon, are tough and hard and are used for springs, tools, and cutlery.

Many types of steel also contain elements in addition to iron and carbon. Such steels are often called *alloy steels*, and they can be viewed as being mixed interstitial (carbon) and substitutional (other metals) alloys. Bicycle frames, for example, are constructed from a wide variety of alloy steels. The compositions of the two brands of steel tubing most commonly used in expensive racing bicycles are given in Table 10.4.

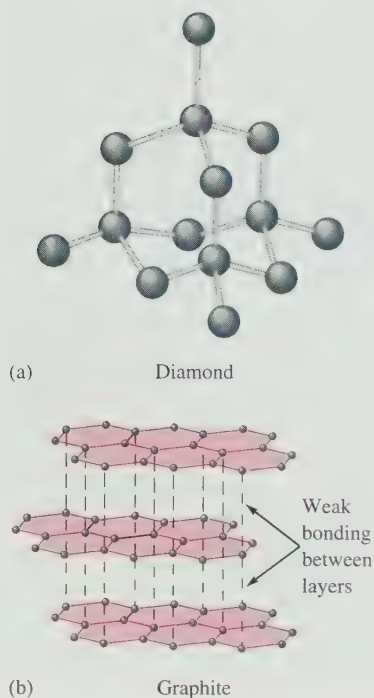
10.5 Carbon and Silicon: Network Atomic Solids

Many atomic solids contain strong directional covalent bonds to form a solid that might best be viewed as a “giant molecule.” We call these substances **network solids**. In contrast to metals, these materials are typically brittle and do not efficiently conduct heat or electricity. To illustrate network solids, in this section we will discuss two very important elements, carbon and silicon, and some of their compounds.

The two most common forms of carbon, diamond and graphite, are typical network solids. In diamond, the hardest naturally occurring substance, each carbon atom is surrounded by a tetrahedral arrangement of other carbon atoms to form a huge molecule [see Fig. 10.22(a)]. This structure is stabilized by covalent bonds, which, in terms of the localized electron model, are formed by the overlap of sp^3 hybridized carbon atomic orbitals.

It is also useful to consider the bonding among the carbon atoms in diamond in terms of the molecular orbital model. Energy-level diagrams for diamond and a typical metal are given in Fig. 10.23. Recall that the conductivity of metals can be explained by postulating that electrons are excited from filled levels into the very near empty levels, or conduction bands. However, note that in the energy-level diagram for diamond there is a *large gap between the filled and the empty levels*. This means that electrons cannot be transferred easily to the empty conduction bands. As a result, diamond is not expected to be a good electrical conductor. In fact, this prediction of the model agrees exactly with the observed behavior of diamond, which is known to be an electrical insulator—it does not conduct an electric current.

Graphite is very different from diamond. While diamond is hard, basically colorless, and an insulator, graphite is slippery, black, and a conductor. These differences, of course, arise from the differences in bonding in the two types of solids. In contrast to the tetrahedral arrangement of carbon atoms in diamond, the structure of graphite is based on layers of carbon atoms arranged in fused six-membered rings, as shown in Fig. 10.22(b). Each carbon atom in a particular layer of graphite is surrounded by the three other carbon atoms in a trigonal planar arrangement with 120-degree bond angles. The localized electron model predicts sp^2 hybridization in

**FIGURE 10.22**

The structures of diamond and graphite. In each case only a small part of the entire structure is shown.



Graphite and diamond, two forms of carbon.

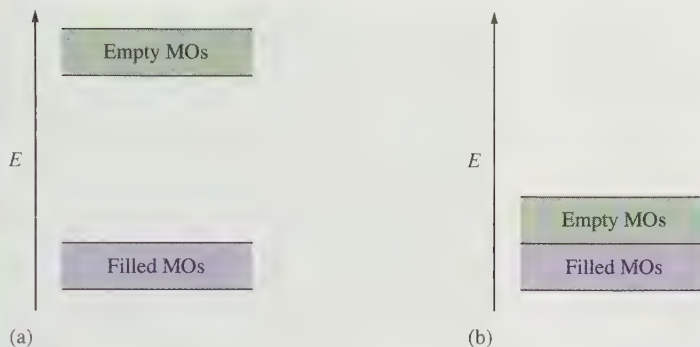


FIGURE 10.23

Partial representation of the molecular orbital energies in (a) diamond and (b) a typical metal.

this case. The three sp^2 orbitals on each carbon are used to form σ bonds with three other carbon atoms. One $2p$ orbital remains unhybridized on each carbon and is perpendicular to the plane of carbon atoms, as shown in Fig. 10.24. These orbitals combine to form a group of closely spaced π molecular orbitals that are important in two ways. First, they contribute significantly to the stability of the graphite layers because of the π bond formation. Second, the π molecular orbitals with their delocalized electrons account for the electrical conductivity of graphite. These closely spaced orbitals are exactly analogous to the conduction bands found in metal crystals.

Graphite is often used as a lubricant in locks (where oil is undesirable because it collects dirt). The slipperiness that is characteristic of graphite can be explained by noting that graphite has very strong bonding *within* the layers of carbon atoms but little bonding *between* the layers (the valence electrons are all used to form σ and π bonds among carbons within the layers). This arrangement allows the layers to slide past one another quite readily. Graphite's layered structure is shown in Fig. 10.25. This is in contrast to diamond, which has uniform bonding in all directions in the crystal.

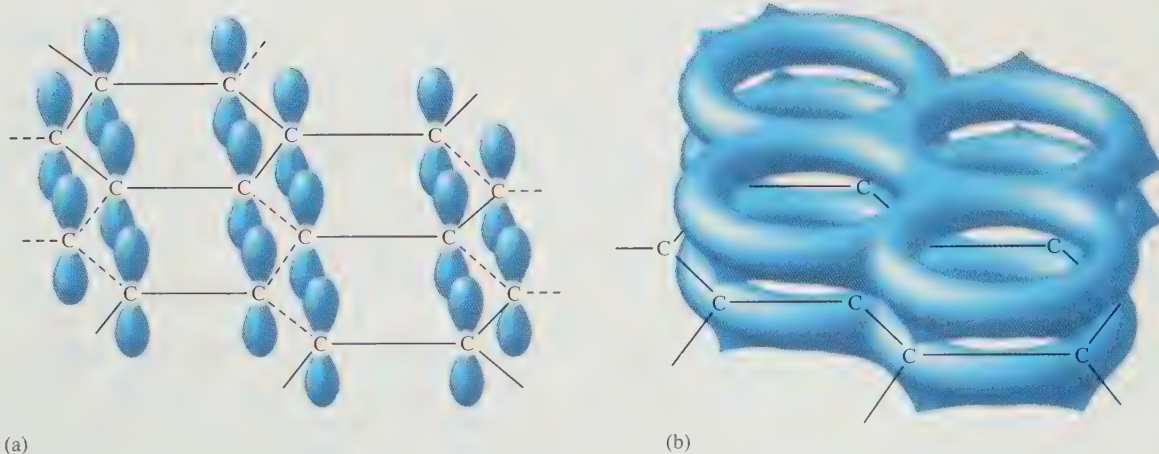


FIGURE 10.24

The p orbitals (a) perpendicular to the plane of the carbon ring system in graphite can combine to form (b) an extensive π -bonding network.

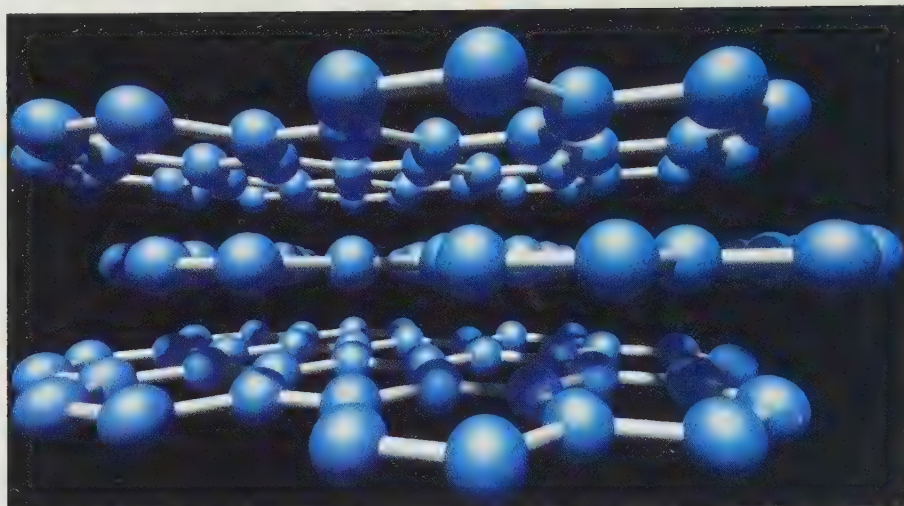


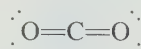
FIGURE 10.25
Graphite consists of layers of carbon atoms.

Because of their extreme hardness, diamonds are used extensively in industrial cutting implements. Thus it is desirable to convert cheaper graphite to diamond. As we might expect from the higher density of diamond (3.5 g/cm^3) compared with that of graphite (2.2 g/cm^3), this transformation can be accomplished by applying very high pressures to graphite. The application of 150,000 atm of pressure at 2800°C converts graphite virtually completely to diamond. The high temperature is required to break the strong bonds in graphite so the rearrangement can occur.

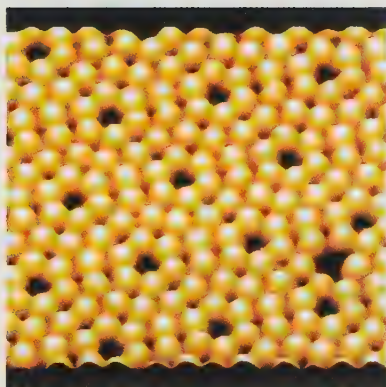
Silicon is an important constituent of the compounds that make up the earth's crust. In fact, silicon is to geology as carbon is to biology. Just as carbon compounds are the basis for most biologically significant systems, silicon compounds are fundamental to most of the rocks, sands, and soils found in the earth's crust. However, although carbon and silicon are next to each other in Group 4A of the periodic table, the carbon-based compounds of biology and the silicon-based compounds of geology have markedly different structures. Carbon compounds typically contain long strings of carbon-carbon bonds, whereas the most stable silicon compounds involve chains with silicon-oxygen bonds.

The fundamental silicon-oxygen compound is **silica**, which has the empirical formula SiO_2 . Knowing the properties of the similar compound carbon dioxide, one might expect silica to be a gas that contains discrete SiO_2 molecules. In fact, nothing could be further from the truth—quartz and some types of sand are typical of the materials composed of silica. What accounts for this difference? The answer lies in the bonding.

Recall that the Lewis structure of CO_2 is



and that each $\text{C}=\text{O}$ bond can be viewed as a combination of a σ bond involving a carbon sp hybrid orbital and a π bond involving a carbon $2p$ orbital. On the contrary, silicon cannot use its valence $3p$ orbitals to form strong π bonds with oxygen, mainly because of the larger size of the silicon atom and its orbitals, which results in less effective overlap with the smaller oxygen orbitals. Therefore, instead of forming π bonds, the silicon atom satisfies the octet rule by forming single bonds with four oxygen atoms, as shown in the representation of the structure of quartz in Fig. 10.26. Note that each silicon atom is at the center of a tetrahedral arrangement



Computer-generated model of silica.

The bonding in the CO_2 molecule was described in Section 9.1.

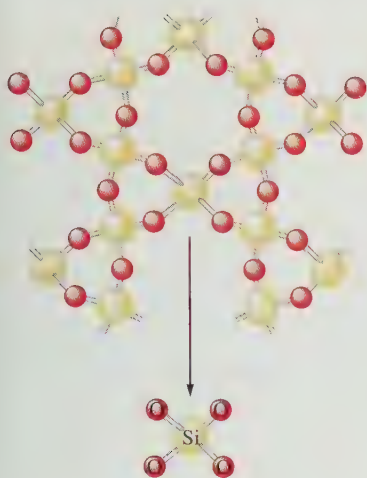


FIGURE 10.26
(top) The structure of quartz (empirical formula SiO_2). Quartz contains chains of SiO_4 tetrahedra (bottom) that share oxygen atoms.

of oxygen atoms, which are shared with other silicon atoms. Although the empirical formula for quartz is SiO_2 , the structure is based on a *network* of SiO_4 tetrahedra with shared oxygen atoms rather than discrete SiO_2 molecules. It is obvious that the differing abilities of carbon and silicon to form π bonds with oxygen have profound effects on the structures and properties of CO_2 and SiO_2 .

Compounds closely related to silica and found in most rocks, soils, and clays are the **silicates**. Like silica, the silicates are based on interconnected SiO_4 tetrahedra. However, in contrast to silica, where the O/Si ratio is 2:1, silicates have O/Si ratios greater than 2:1 and contain silicon–oxygen *anions*. This means that to form the neutral solid silicates, cations are needed to balance the excess negative charge. In other words, silicates are salts containing metal cations and polyatomic silicon–oxygen anions. Examples of important silicate anions are shown in Fig. 10.27.

When silica is heated above its melting point (about 1600°C) and cooled rapidly, an amorphous solid called a **glass** results (see Fig. 10.28). Note that a glass contains a good deal of disorder, in contrast to the crystalline nature of quartz. Glass more closely resembles a very viscous solution than it does a crystalline solid. Common glass results when substances such as Na_2CO_3 are added to the silica melt, which is then cooled. The properties of glass can be varied greatly by varying the additives. For example, addition of B_2O_3 produces a glass (called *borosilicate glass*) that expands and contracts little under large temperature changes. Thus it is useful for labware and cooking utensils. The most common brand name for this glass is Pyrex. The addition of K_2O produces an especially hard glass that can be ground to

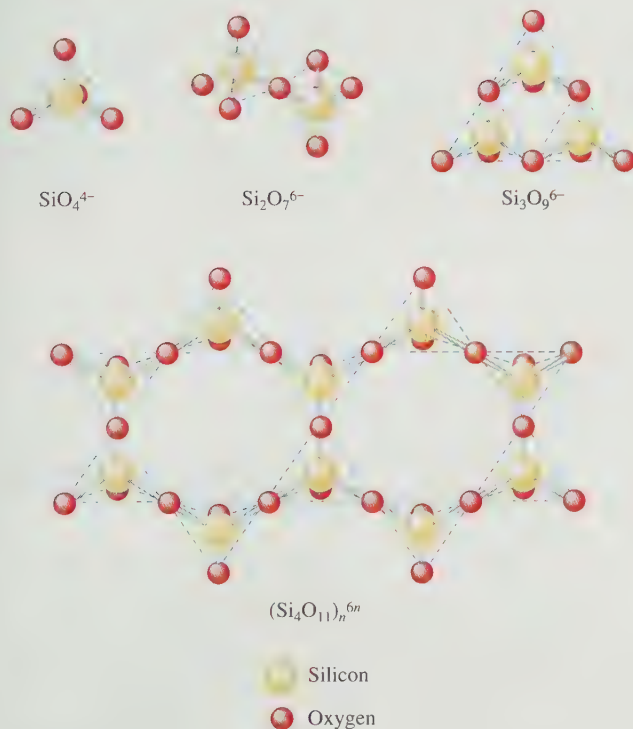


FIGURE 10.27
Examples of silicate anions, all of which are based on SiO_4^{4-} tetrahedra.

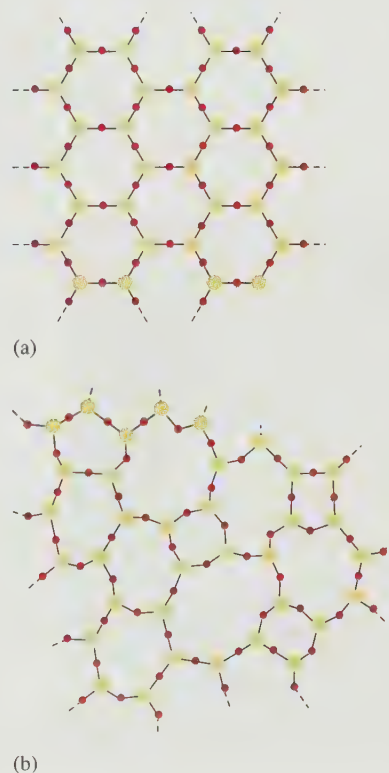
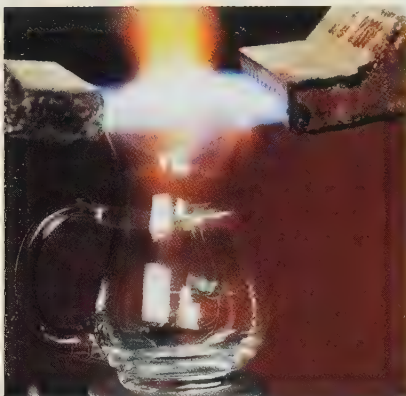


FIGURE 10.28
Two-dimensional representations of (a) a quartz crystal and (b) a quartz glass.

TABLE 10.5 Compositions of Some Common Types of Glass

Type of Glass	Percentages of Various Components						
	SiO ₂	CaO	Na ₂ O	B ₂ O ₃	Al ₂ O ₃	K ₂ O	MgO
Window (soda-lime glass)	72	11	13	—	0.3	3.8	—
Cookware (aluminosilicate glass)	55	15	—	—	20	—	10
Heat-resistant (borosilicate glass)	76	3	5	13	2	0.5	—
Optical	69	12	6	0.3	—	12	—



A glass pitcher being manufactured.

the precise shapes needed for eyeglass and contact lenses. The compositions of several types of glass are shown in Table 10.5.

Ceramics

Ceramics are typically made from clays (which contain silicates) and hardened by firing at high temperatures. Ceramics are nonmetallic materials that are strong, brittle, and resistant to heat and attack by chemicals.

Like glass, ceramics are based on silicates, but with that the resemblance ends. Glass can be melted and remelted as often as desired, but once a ceramic has been hardened, it is resistant to extremely high temperatures. This behavior results from the very different structures of glasses and ceramics. A glass is a *homogeneous*, non-crystalline “frozen solution,” and a ceramic is *heterogeneous*. A ceramic contains two phases: minute crystals of silicates that are suspended in a glassy cement.

To understand how ceramics harden, it is necessary to know something about the structure of clays. Clays are formed by the weathering action of water and carbon dioxide on the mineral feldspar, which is a mixture of silicates with empirical formulas such as $K_2O \cdot Al_2O_3 \cdot 6SiO_2$ and $Na_2O \cdot Al_2O_3 \cdot 6SiO_2$. Feldspar is really an *aluminosilicate* in which aluminum as well as silicon atoms are part of the oxygen-bridged polyanion. The weathering of feldspar produces kaolinite, consisting of tiny thin platelets with the empirical formula $Al_2Si_2O_5(OH)_4$. When dry, the platelets cling together; when water is present, they can slide over one another, giving clay its plasticity. As clay dries, the platelets begin to interlock again. When the remaining water is driven off during firing, the silicates and cations form a glass that binds the tiny crystals of kaolinite.

Ceramics have a very long history. Rocks, which are natural ceramic materials, served as the earliest tools. Later, clay vessels dried in the sun or baked in fires served as containers for food and water. These early vessels were no doubt crude and quite porous. With the discovery of glazing, which probably occurred about 3000 B.C. in Egypt, pottery became more serviceable as well as more beautiful. Prized porcelain is essentially the same material as crude earthenware, but specially selected clays and glazings are used for porcelain and the clay object is fired at a very high temperature.

Although ceramics have been known since antiquity, they are not obsolete materials. On the contrary, ceramics constitute one of the most important classes of “high-tech” materials. Because of their stability at high temperatures and resistance to corrosion, ceramics seem an obvious choice for constructing jet and automobile engines in which the greatest fuel efficiencies are possible at very high temperatures. But ceramics are brittle—they break rather than bend—which limits their usefulness. However, more flexible ceramics can be obtained by adding small amounts



An artist paints a ceramic vase before glazing.

CHEMICAL IMPACT

Golfing with Glass

You probably can guess what material traditionally was used to construct the “woods” used in golf. Modern technology has changed things. Like the bats used in college baseball, most “woods” are now made of metal. While bats are made of aluminum, golf club heads are often made of stainless steel or titanium.

Metals and their alloys usually form crystals that contain highly ordered arrangements of atoms. However, a company called Liquidmetal Golf of Laguna Niguel, California, has begun producing golf clubs containing glass—metallic glass. The company has found that when molten mixtures of titanium, zirconium, nickel, beryllium, and copper are cooled, they solidify, forming a glass. Unlike crystalline materials that contain a regular array of atoms, glasses are amorphous—the atoms are randomly scattered throughout the solid.

These golf clubs with metallic glass inserts have some unusual characteristics. Golfers who have tried the clubs say they combine hardness with a “soft feel.” Studies show that the glass transfers more of the energy of the golf swing to the ball with less impact to the golfer’s hands than with regular metal woods.

One of the fortunate properties of this five-component metallic glass (invented in 1992 by William L. Johnson and Atakan Peker at the California Institute of Technology) is that it can be cooled relatively slowly to form the glass. This allows manufacture of relatively large glass objects such as inserts for golf club heads. Most mixtures of metals that form glasses must be cooled very rapidly to obtain the glass, which results in tiny particles of glass leading to powders.



Golf clubs with a titanium shell and metallic glass inserts.

David S. Lee, head of manufacturing at Liquidmetal Golf, says that golf clubs were an obvious first application for this five-component glass because golfers are used to paying high prices for clubs that employ new technology. Liquidmetal Golf is now looking for other applications of this new glass. How about glass bicycle frames?

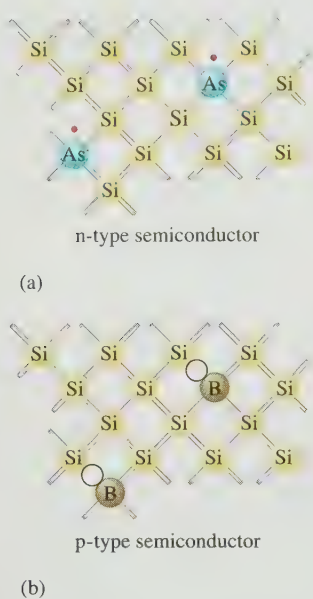


Visualization: Magnetic Levitation by a Superconductor

of organic polymers. Taking their cue from natural “organoceramics” such as teeth and shells of sea creatures that contain small amounts of organic polymers, materials scientists have found that incorporating tiny amounts of long organic molecules into ceramics as they form produces materials that are much less subject to fracture. These materials should be useful for lighter, more durable engine parts, as well as for flexible superconducting wire and microelectronic devices. In addition, these organoceramics hold great promise for prosthetic devices such as artificial bones.

Semiconductors

Elemental silicon has the same structure as diamond, as might be expected from its position in the periodic table (in Group 4A directly under carbon). Recall that in diamond there is a large energy gap between the filled and empty molecular orbitals (see Fig. 10.23). This gap prevents excitation of electrons to the empty molecular

**FIGURE 10.29**

(a) A silicon crystal doped with arsenic, which has one more valence electron than silicon. (b) A silicon crystal doped with boron, which has one less electron than silicon.

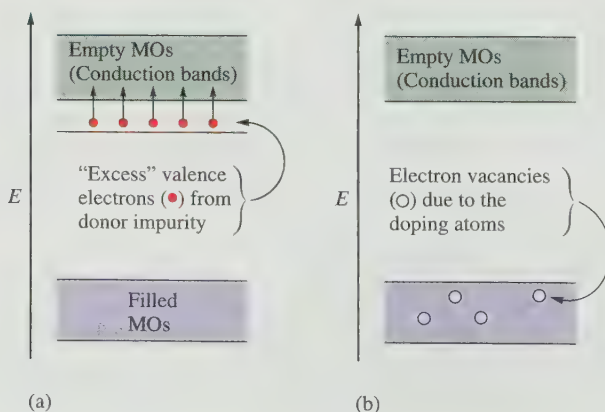
Electrons must be in singly occupied molecular orbitals to conduct a current.

orbitals (conduction bands) and makes diamond an insulator. In silicon the situation is similar, but the energy gap is smaller. A few electrons can cross the gap at 25°C, making silicon a **semiconducting element**, or **semiconductor**. In addition, at higher temperatures, where more energy is available to excite electrons into the conduction bands, the conductivity of silicon increases. This is typical behavior for a semiconducting element and is in contrast to that of metals, whose conductivity decreases with increasing temperature.

The small conductivity of silicon can be enhanced at normal temperatures if the silicon crystal is *doped* with certain other elements. For example, when a small fraction of silicon atoms is replaced by arsenic atoms, each having *one more* valence electron than silicon, extra electrons become available for conduction, as shown in Fig. 10.29(a). This produces an **n-type semiconductor**, a substance whose conductivity is increased by doping it with atoms having more valence electrons than the atoms in the host crystal. These extra electrons lie close in energy to the conduction bands and can be easily excited into these levels, where they can conduct an electric current [see Fig. 10.30(a)].

We also can enhance the conductivity of silicon by doping the crystal with an element such as boron, which has only three valence electrons, *one less* than silicon. Because boron has one less electron than is required to form the bonds with the surrounding silicon atoms, an electron vacancy, or *hole*, is created, as shown in Fig. 10.29(b). As an electron fills this hole, it leaves a new hole, and this process can be repeated. Thus the hole advances through the crystal in a direction opposite to movement of the electrons jumping to fill the hole. Another way of thinking about this phenomenon is that in pure silicon each atom has four valence electrons and the low-energy molecular orbitals are exactly filled. Replacing silicon atoms with boron atoms leaves vacancies in these molecular orbitals, as shown in Fig. 10.30(b). This means that there is only one electron in some of the molecular orbitals, and these unpaired electrons can function as conducting electrons. Thus the substance becomes a better conductor. When semiconductors are doped with atoms having fewer valence electrons than the atoms of the host crystal, they are called **p-type semiconductors**, so named because the positive holes can be viewed as the charge carriers.

Most important applications of semiconductors involve connection of a p-type and an n-type to form a **p-n junction**. Figure 10.31(a) shows a typical junction; the red dots represent excess electrons in the n-type semiconductor, and the white circles represent holes (electron vacancies) in the p-type semiconductor. At the junction, a

**FIGURE 10.30**

Energy-level diagrams for (a) an n-type semiconductor and (b) a p-type semiconductor.

small number of electrons migrate from the n-type region into the p-type region, where there are vacancies in the low-energy molecular orbitals. The effect of these migrations is to place a negative charge on the p-type region (since it now has a surplus of electrons) and a positive charge on the n-type region (since it has lost electrons, leaving holes in its low-energy molecular orbitals). This charge buildup, called the *contact potential*, or *junction potential*, prevents further migration of electrons.

Now suppose an external electric potential is applied by connecting the negative terminal of a battery to the p-type region and the positive terminal to the n-type region. The situation represented in Fig. 10.31(b) results. Electrons are drawn toward the positive terminal, and the resulting holes move toward the negative terminal—exactly opposite to the natural flow of electrons at the p–n junction. The junction resists the imposed current flow in this direction and is said to be under *reverse bias*. No current flows through the system.

On the other hand, if the battery is connected so that the negative terminal is connected to the n-type region and the positive terminal is connected to the p-type region [Fig. 10.31(c)], the movement of electrons (and holes) is in the favored direction. The junction has low resistance, and a current flows easily. The junction is said to be under *forward bias*.

A p–n junction makes an excellent *rectifier*, a device that produces a pulsating direct current (flows in one direction) from alternating current (flows in both directions alternately). When placed in a circuit where the potential is constantly reversing, a p–n junction transmits current only under forward bias, thus converting the alternating current to direct current. Radios, computers, and other electronic

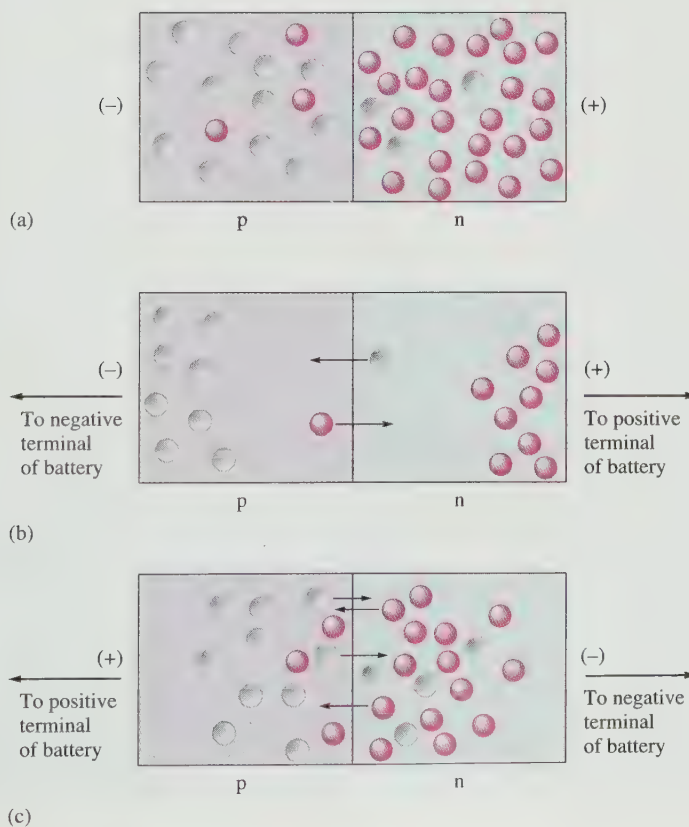


FIGURE 10.31

The p–n junction involves the contact of a p-type and an n-type semiconductor. (a) The charge carriers of the p-type region are holes (●). In the n-type region the charge carriers are electrons (●). (b) No current flows (reverse bias). (c) Current readily flows (forward bias). Note that each electron that crosses the boundary leaves a hole behind. Thus the electrons and the holes move in opposite directions.

Transistors and Printed Circuits

Transistors have had an immense impact on the technology of electronic devices for which signal amplification is needed, such as communications equipment and computers. Before the invention of the transistor at Bell Laboratories in 1947, amplification was provided exclusively by vacuum tubes, which were both bulky and unreliable. The first electronic digital computer, ENIAC, built at the University of Pennsylvania, had 19,000 vacuum tubes and consumed 150,000 watts of electricity. Because of the discovery and development of the transistor and the printed circuit, a hand-held calculator run by a small battery has the same computing power as ENIAC.

A *junction transistor* is made by joining n-type and p-type semiconductors so as to form an n-p-n or a p-n-p junction. The former type is shown in Fig. 10.32. In this diagram the input signal (to be amplified) occurs in circuit 1, which has a small resistance and a forward-biased n-p junction (junction 1). As the voltage of the input signal to this circuit varies, the current in the circuit varies, which means there is a change in the number of electrons crossing the n-p junction. Circuit 2 has a relatively large resistance and is under reverse bias. The key to operation of the transistor is that current only flows in circuit 2 when electrons crossing junction 1 also cross junction 2 and travel to the positive terminal. Since the current in circuit 1 determines the number of electrons crossing junction 1, the number of electrons available to cross junction 2 is also directly proportional to the current in circuit 1. The current in circuit 2 therefore varies depending on the current in circuit 1.

The voltage V , current I , and resistance R in a circuit are related by the equation

$$V = IR$$

Since circuit 2 has a large resistance, a given current in circuit 2 produces a larger voltage than the same current in circuit 1, which has a small resistance. Thus a signal or variable voltage in circuit 1, such as might be produced by a human voice on a telephone, is reproduced in circuit 2, but with much greater voltage changes. That is, the input signal has been *amplified* by the junction transistor. This device, which has replaced the large vacuum tube, is a tiny component of a printed circuit on a silicon chip.

Silicon chips are really “planar” transistors constructed from thin layers of n-type and p-type regions connected by conductors. A chip less than 1 cm wide can contain hundreds of printed circuits and be used in computers, radios, and televisions.

A printed circuit has many n-p-n junction transistors. Fig. 10.33 illustrates the formation of one transistor area. The chip begins as a thin wafer of silicon that has been doped with an n-type impurity. A protective layer of silicon dioxide is then produced on the wafer by exposing it in a furnace to an oxidizing atmosphere. The next step is to produce a p-type semiconductor. To do this, the surface of the oxide is covered by a polymeric photoresist, as shown in Fig. 10.33(a). A template that only allows light to shine through in selected areas is then placed on top [Fig. 10.33(b)], and light is shown

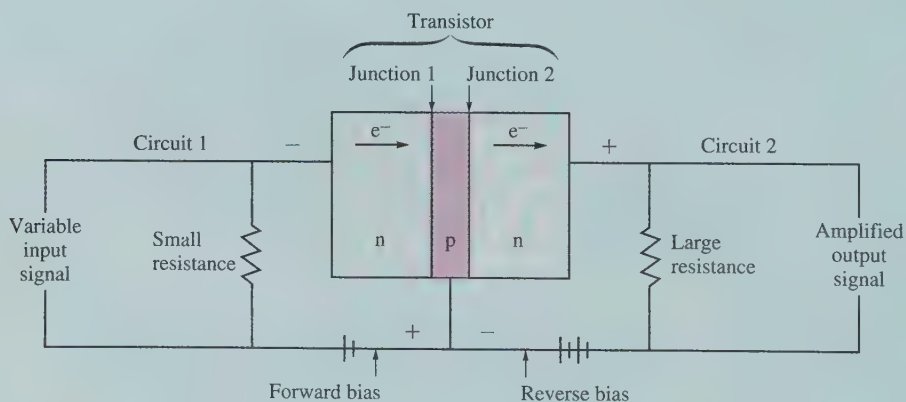


FIGURE 10.32

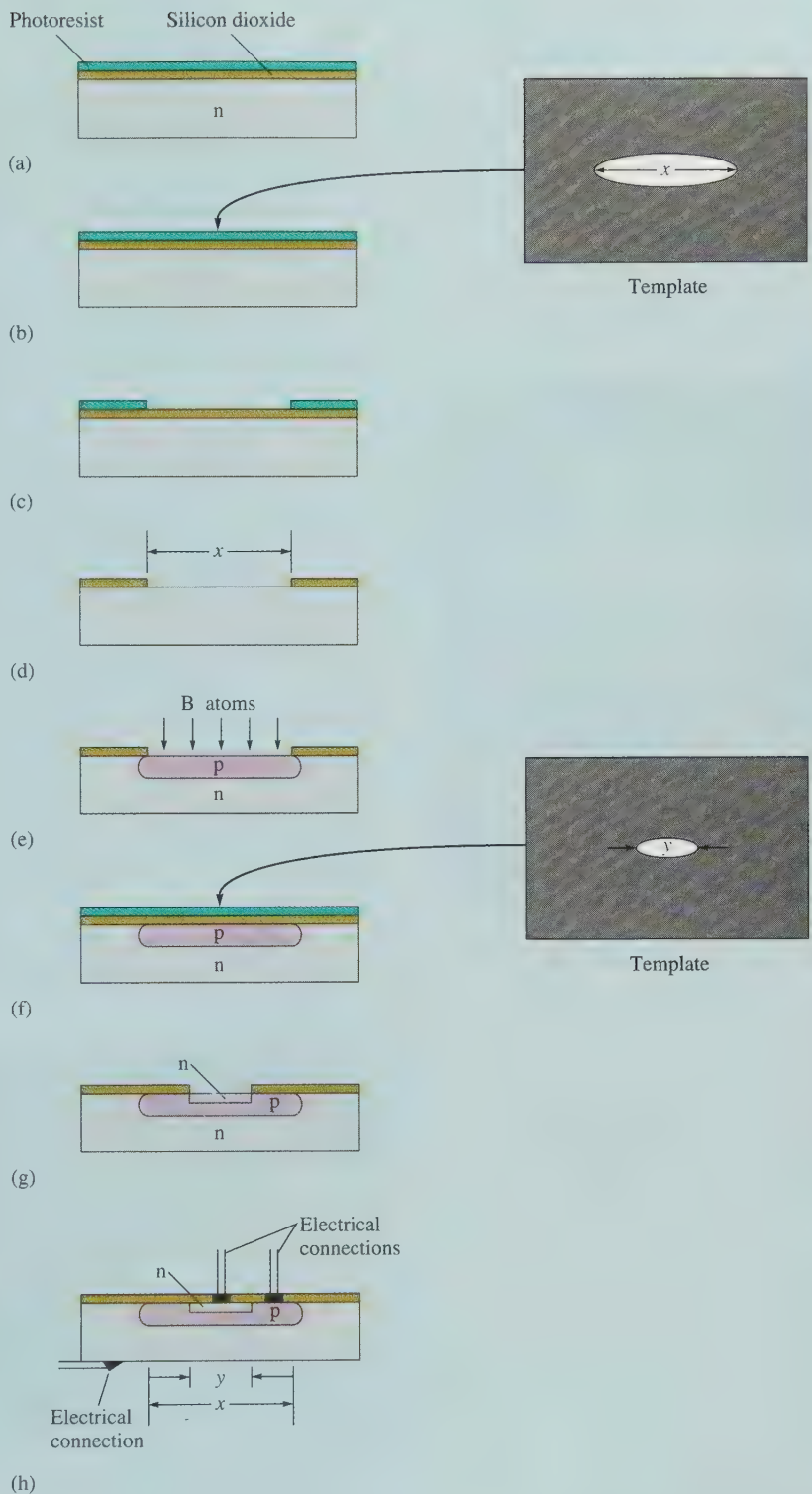
A schematic of two circuits connected by a transistor. The signal in circuit 1 is amplified in circuit 2.

on the chip. The photoresist that has been exposed to light undergoes a chemical change that causes its solubility to be different from the unexposed photoresist. The exposed wax is dissolved using selective solvents [Fig. 10.33(c)], and the exposed area is treated with an etching solution to dissolve the oxide coating [Fig. 10.33(d)]. When the remaining photoresist is dissolved, the silicon wafer has its oxide coating intact except at the one spot (of diameter x), as shown in Fig. 10.33(d).

Exposing the wafer to a p-type impurity such as boron at about 1000°C causes a p-type semiconductor area to be formed in the exposed spot as the boron atoms diffuse into the silicon crystal [Fig. 10.33(e)]. Next, to form a small n-type area in the center of the p-type region, the wafer is again placed in the oxidizing furnace to be re-coated over its entire surface with oxide. Then a new photoresist covering is applied, which is illuminated through a template with a transparent area indicated by y [Fig. 10.33(f)]. The photoresist and oxide are then removed from the illuminated area, and the wafer is exposed to an n-type impurity to form a small n-type region as shown in Fig. 10.33(g). Next, conductors are layered onto the chip giving the finished transistor [Fig. 10.33(h)], which has two circuits connected through an n-p-n junction (see Fig. 10.32). This transistor then becomes a part of a large circuit layered onto the chip and interconnected by conductors.

The method given here for producing a printed circuit does not represent the latest technology in this field. The manufacture of printed circuits is a highly competitive business, and changes in methodology occur almost daily.

FIGURE 10.33
The steps for forming a transistor in a crystal of initially pure silicon.



Printed circuits are discussed in the Chemical Impact feature on page 476.

devices formerly used bulky, unreliable vacuum tubes as rectifiers. The p-n junction has revolutionized electronics; modern solid-state components contain p-n junctions in printed circuits.

10.6 Molecular Solids

So far we have considered solids in which atoms occupy the lattice positions. In some of these substances (network solids), the solid can be considered to be one giant molecule. In addition, there are many types of solids that contain discrete molecular units at each lattice position. A common example is ice, where the lattice positions are occupied by water molecules [see Fig. 10.12(c)]. Other examples are dry ice (solid carbon dioxide), some forms of sulfur that contain S_8 molecules [Fig. 10.34(a)], and certain forms of phosphorus that contain P_4 molecules [Fig. 10.34(b)]. These substances are characterized by strong covalent bonding *within* the molecules but relatively weak forces *between* the molecules. For example, it takes only 6 kJ of energy to melt 1 mole of solid water (ice) because only intermolecular (H_2O-H_2O) interactions must be overcome. However, 470 kJ of energy is required to break 1 mole of covalent O—H bonds. The differences between the covalent bonds within the molecules and the forces between the molecules are apparent from the comparison of the interatomic and intermolecular distances in solids shown in Table 10.6.

The forces that exist among the molecules in a molecular solid depend on the nature of the molecules. Many molecules such as CO_2 , I_2 , P_4 , and S_8 have no dipole moment, and the intermolecular forces are London dispersion forces. Because these forces are often relatively small, we might expect all these substances to be gaseous at 25°C, as is the case for carbon dioxide. However, as the size of the molecules increases, the London forces become quite large, causing many of these substances to be solids at 25°C.



A “steaming” piece of dry ice.

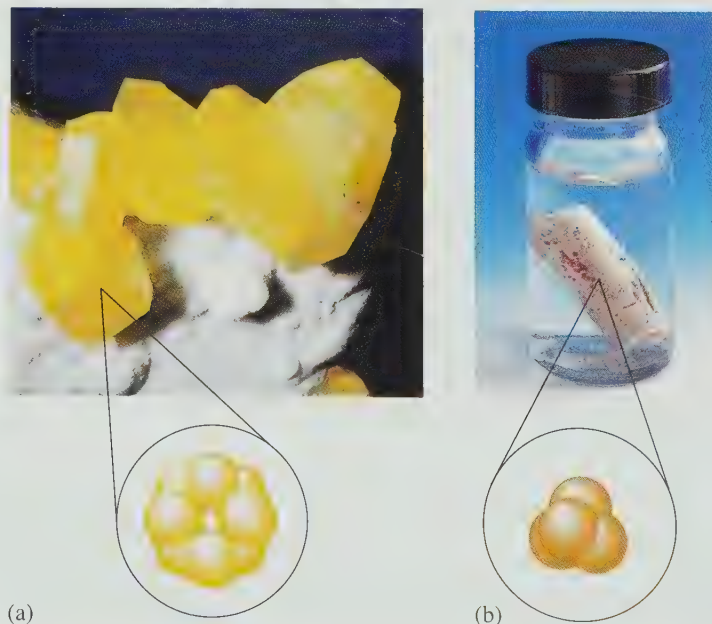


FIGURE 10.34

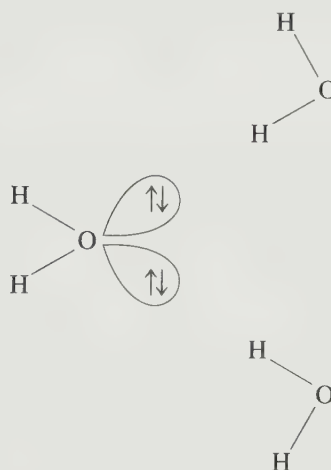
(a) Sulfur crystals (yellow) contain S_8 molecules. (b) White phosphorus (containing P_4 molecules) is so reactive with the oxygen in air that it must be stored under water.

TABLE 10.6 Comparison of Atomic Separations Within Molecules (Covalent Bonds) and Between Molecules (Intermolecular Interactions)

Solid	Distance Between Atoms in Molecule*	Closest Distance Between Molecules in the Solid
P ₄	220 pm	380 pm
S ₈	206 pm	370 pm
Cl ₂	199 pm	360 pm

*The shorter distances within the molecules indicate stronger bonding.

When molecules do have dipole moments, their intermolecular forces are significantly greater, especially when hydrogen bonding is possible. Water molecules are particularly well suited to interact with each other because each molecule has two polar O—H bonds and two lone pairs on the oxygen atom. This can lead to the association of four hydrogen atoms with each oxygen: two by covalent bonds and two by dipole forces:

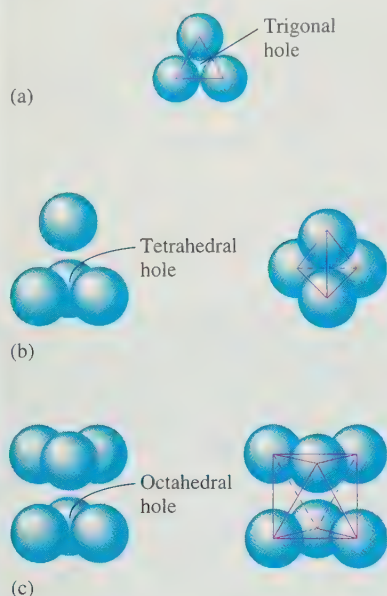


Note the two relatively short covalent oxygen–hydrogen bonds and the two longer oxygen–hydrogen dipole interactions that can be seen in the ice structure in Fig. 10.12(c).

10.7 Ionic Solids

Ionic solids are stable, high-melting substances held together by the strong electrostatic forces that exist between oppositely charged ions. The principles governing the structures of ionic solids were introduced in Section 8.5. In this section we will review and extend these principles.

The structures of most binary ionic solids, such as sodium chloride, can be explained by the closest packing of spheres. Typically, the larger ions, usually the anions, are packed in one of the closest packing arrangements (hcp or ccp), and the smaller cations fit into holes among the closest packed anions. The packing is done in a way that maximizes the electrostatic attractions among oppositely charged ions and minimizes the repulsions among ions with like charges.

**FIGURE 10.35**

The holes that exist among closest packed uniform spheres. (a) The trigonal hole formed by three spheres in a given plane. (b) The tetrahedral hole formed when a sphere occupies a dimple formed by three spheres in an adjacent layer. (c) The octahedral hole formed by six spheres in two adjacent layers.

Closest packed structures contain twice as many tetrahedral holes as packed spheres. Closest packed structures contain the same number of octahedral holes as packed spheres.

There are three types of holes in closest packed structures:

1. Trigonal holes are formed by three spheres in the same layer [Fig. 10.35(a)].
2. Tetrahedral holes are formed when a sphere sits in the dimple of three spheres in an adjacent layer [Fig. 10.35(b)].
3. Octahedral holes are formed between two sets of three spheres in adjoining layers of the closest packed structures [Fig. 10.35(c)].

For spheres of a given diameter, the holes increase in size in the order

$$\text{trigonal} < \text{tetrahedral} < \text{octahedral}$$

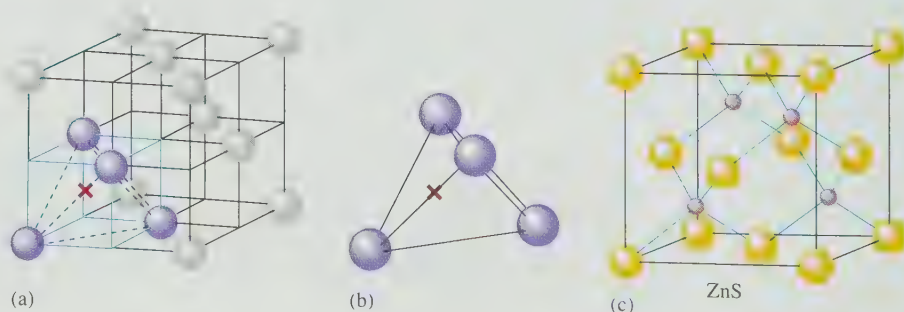
In fact, trigonal holes are so small that they are never occupied in binary ionic compounds. Whether the tetrahedral or octahedral holes in a given binary ionic solid are occupied depends mainly on the *relative* sizes of the anion and cation. For example, in zinc sulfide the S^{2-} ions (ionic radius = 180 pm) are arranged in a cubic closest packed structure with the smaller Zn^{2+} ions (ionic radius = 70 pm) in the tetrahedral holes. The locations of the tetrahedral holes in the face-centered cubic unit cell of the ccp structure are shown in Fig. 10.36(a). Note from this figure that there are eight tetrahedral holes in the unit cell. Also recall from the discussion in Section 10.4 that there are four net spheres in the face-centered cubic unit cell. Thus there are *twice as many tetrahedral holes as packed anions* in the closest packed structure. Zinc sulfide must have the same number of S^{2-} ions and Zn^{2+} ions to achieve electrical neutrality. Thus in the zinc sulfide structure only *half* the tetrahedral holes contain Zn^{2+} ions, as shown in Fig. 10.36(c).

The structure of sodium chloride can be described in terms of a cubic closest packed array of Cl^- ions with Na^+ ions in all the octahedral holes. The locations of the octahedral holes in the face-centered cubic unit cell are shown in Fig. 10.37(a) on page 482. The easiest octahedral hole to find in this structure is the one at the center of the cube. Note that this hole is surrounded by six spheres, as is required to form an octahedron. The remaining octahedral holes are shared with other unit cells and are more difficult to visualize. However, it can be shown that the number of octahedral holes in the ccp structure is the *same* as the number of packed anions. Figure 10.37(b) shows the structure for sodium chloride that results from Na^+ ions filling all the octahedral holes in a ccp array of Cl^- ions.

A great variety of ionic solids exists. Our purpose in this section is not to give an exhaustive treatment of ionic solids, but to emphasize the fundamental principles governing their structures. As we have seen, the most useful model for explaining the structures of these solids regards the ions as hard spheres that are packed to maximize attractions and minimize repulsions.

FIGURE 10.36

(a) The location (X) of a tetrahedral hole in the face-centered cubic unit cell. (b) One of the tetrahedral holes. (c) The unit cell for ZnS where the S^{2-} ions (yellow) are closest packed with the Zn^{2+} ions (red) in alternating tetrahedral holes.

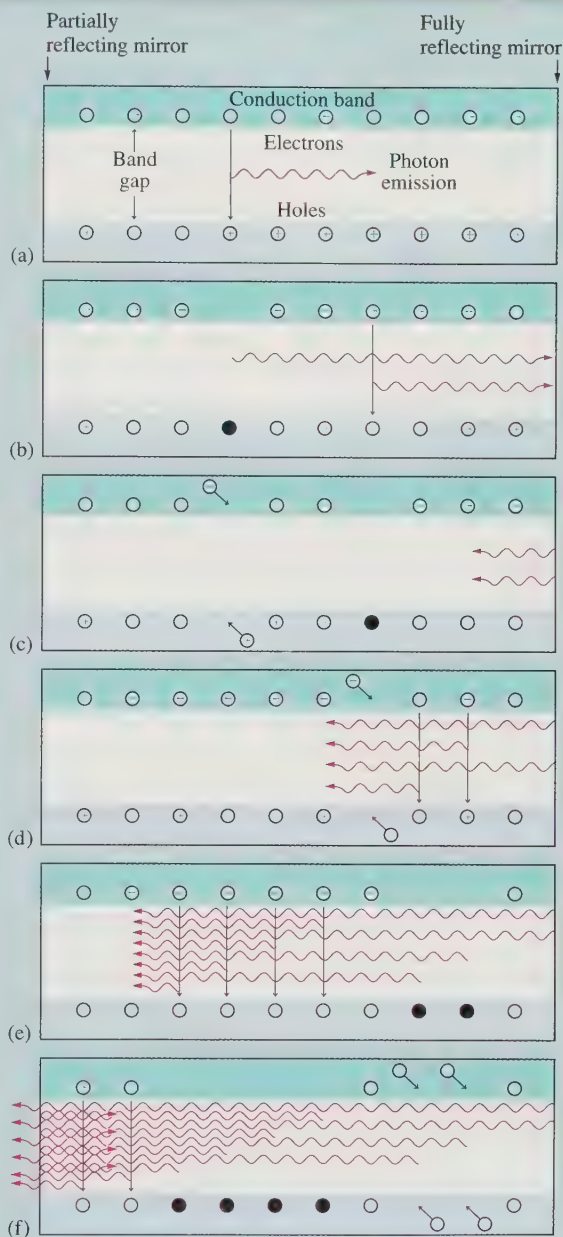


CHEMICAL IMPACT

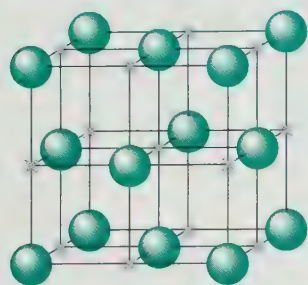
Gallium Arsenide Lasers

Lasers are an essential part of modern life, providing the most efficient way to carry telephone communications by cable, the best quality music using compact disc players, and the most accurate method for reading grocery prices. The laser (the word *lase* is an acronym for “light amplification by stimulated emission”) is a device for producing an intense, coherent beam of light that results when excited electrons release photons as they change to a lower energy state. Excited electrons can return to a lower energy level by spontaneous, random emission of light. However, there is another mechanism in which the emission process is actually stimulated by a passing photon that has the same energy as the emitted photon. This is the phenomenon on which the laser is based. We will have more to say about this presently.

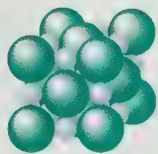
Gallium arsenide is a prominent member of the so-called 3–5 class of semiconductors, those containing elements from Groups 3A and 5A of the periodic table. An n-type semiconductor results when the arsenic-to-gallium ratio is greater than 1. A p-type semiconductor results when gallium is in excess. By carefully controlling the conditions under which a Ga–As semiconductor is made, one can design p–n junctions into the material. At each p–n junction electrons from the n-type region are available to “fall into” holes in the p-type region, producing photons (see the accompanying figure). As the emitted photons travel through the solid, they *stimulate* the emission of additional photons. A mirror at the edge of the solid reflects these photons back through the substance, where they stimulate even more emission events. All these stimulated emissions produce photons with their waves in phase. Thus this process leads to a large number of coherent (in-phase) photons, which proceed out the other end of the solid where a “half-mirror” is placed. This mirror reflects some of the photons and allows the rest to leave as an intense, coherent “laser beam” of light. A current driven through the substance by an applied potential difference provides a continuous supply of electrons (and removes electrons to make new holes) so that the process occurs continuously while the power is on.



SAMPLE EXERCISE 10.3



(a)



(b)

FIGURE 10.37

(a) The locations (gray X) of the octahedral holes in the face-centered cubic unit cell. (b) Representation of the unit cell for solid NaCl. The Cl^- ions (green spheres) have a ccp arrangement with Na^+ ions (gray spheres) in all the octahedral holes. Note that this representation shows the idealized closest packed structure of NaCl. In the actual structure, the Cl^- ions do not quite touch.

Determining the Number of Ions in a Unit Cell

Determine the net number of Na^+ and Cl^- ions in the sodium chloride unit cell.

SOLUTION

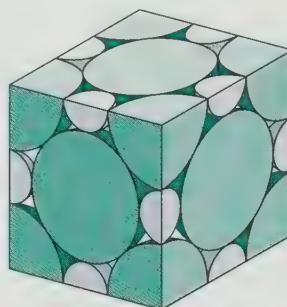
Note from Fig. 10.37(b) that the Cl^- ions are cubic closest packed and thus form a face-centered cubic unit cell. There is a Cl^- ion on each corner and one at the center of each face of the cube. Thus the net number of Cl^- ions present in a unit cell is

$$8\left(\frac{1}{8}\right) + 6\left(\frac{1}{2}\right) = 4$$

The Na^+ ions occupy the octahedral holes located in the center of the cube and midway along each edge. The Na^+ ion in the center of the cube is contained entirely in the unit cell, whereas those on the edges are shared by four unit cells (four cubes share a common edge). Since the number of edges in a cube is 12, the net number of Na^+ ions present is

$$1(1) + 12\left(\frac{1}{4}\right) = 4$$

We have shown that the net number of ions in a unit cell is 4 Na^+ ions and 4 Cl^- ions, which agrees with the 1:1 stoichiometry of sodium chloride.



See Exercises 10.59 through 10.64.

In this chapter we have considered various types of solids. Table 10.7 summarizes these types of solids and some of their properties.

SAMPLE EXERCISE 10.4

Types of Solids

Using Table 10.7, classify each of the following substances according to the type of solid it forms.

- Gold
- Carbon dioxide
- Lithium fluoride
- Krypton

SOLUTION

- Solid gold is an atomic solid with metallic properties.
- Solid carbon dioxide contains nonpolar carbon dioxide molecules and is a molecular solid.

TABLE 10.7 Types and Properties of Solids

Type of Solid:	Atomic			Molecular	Ionic
	Network	Metallic	Group 8A		
Structural Unit:	Atom	Atom	Atom	Molecule	Ion
Type of Bonding:	Directional covalent bonds	Nondirectional covalent bonds involving electrons that are delocalized throughout the crystal	London dispersion forces	Polar molecules: dipole–dipole interactions Nonpolar molecules: London dispersion forces	Ionic
Typical Properties:	Hard High melting point Insulator	Wide range of hardness Wide range of melting points Conductor	Very low melting point	Soft Low melting point Insulator	Hard High melting point Insulator
Examples:	Diamond	Silver Iron Brass	Argon(s)	Ice (solid H ₂ O) Dry ice (solid CO ₂)	Sodium chloride Calcium fluoride

- c. Solid lithium fluoride contains Li⁺ and F[−] ions and is a binary ionic solid.
- d. Solid krypton contains krypton atoms that can interact only through London dispersion forces. It is an atomic solid but has properties characteristic of a molecular solid with nonpolar molecules.

See Exercises 10.67 and 10.68.

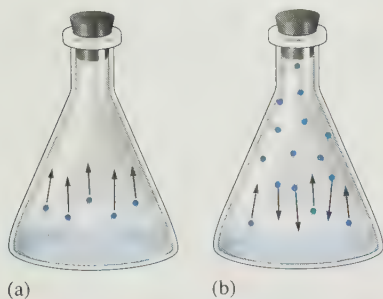
10.8 Vapor Pressure and Changes of State

Now that we have considered the general properties of the three states of matter, we can explore the processes by which matter changes state. One very familiar example of a change in state occurs when a liquid evaporates from an open container. This is clear evidence that the molecules of a liquid can escape the liquid's surface and form a gas, a process called **vaporization**, or **evaporation**. Vaporization is endothermic because energy is required to overcome the relatively strong intermolecular forces in the liquid. The energy required to vaporize 1 mole of a liquid at a pressure of 1 atm is called the **heat of vaporization**, or the **enthalpy of vaporization**, and is usually symbolized as ΔH_{vap} .

The endothermic nature of vaporization has great practical significance; in fact, one of the most important roles that water plays in our world is to act as a coolant. Because of the strong hydrogen bonding among its molecules in the liquid state, water has an unusually large heat of vaporization (40.7 kJ/mol). A significant portion of the sun's energy that reaches earth is spent evaporating water from the oceans, lakes, and rivers rather than warming the earth. The vaporization of water is also crucial to the body's temperature-control system through evaporation of perspiration.

Vapor is the usual term for the gas phase of a substance that exists as a solid or liquid at 25°C and 1 atm.

ΔH_{vap} for water at 100°C is 40.7 kJ/mol.

**FIGURE 10.38**

Behavior of a liquid in a closed container. (a) Initially, net evaporation occurs as molecules are transferred from the liquid to the vapor phase, so the amount of liquid decreases. (b) As the number of vapor molecules increases, the rate of return to the liquid (condensation) increases, until finally the rate of condensation equals the rate of evaporation. The system is at equilibrium, and no further changes occur in the amounts of vapor or liquid.

A system at equilibrium is dynamic on the molecular level but shows no macroscopic changes.

Vapor Pressure

When a liquid is placed in a closed container, the amount of liquid at first decreases but eventually becomes constant. The decrease occurs because there is an initial net transfer of molecules from the liquid to the vapor phase (Fig. 10.38). This evaporation process occurs at a constant rate at a given temperature (see Fig. 10.39). However, the reverse process is different. Initially, as the number of vapor molecules increases, so does the rate of return of these molecules to the liquid. The process by which vapor molecules re-form a liquid is called **condensation**. Eventually, enough vapor molecules are present above the liquid so that the rate of condensation equals the rate of evaporation (see Fig. 10.39). *At this point no further net change occurs in the amount of liquid or vapor because the two opposite processes exactly balance each other; the system is at equilibrium.* Note that this system is highly *dynamic* on the molecular level—molecules are constantly escaping from and entering the liquid at a high rate. However, there is no *net* change because the two opposite processes just *balance* each other.

The pressure of the vapor present at equilibrium is called the **equilibrium vapor pressure**, or more commonly, the **vapor pressure** of the liquid. A simple barometer can measure the vapor pressure of a liquid, as shown in Fig. 10.40(a). The liquid is injected at the bottom of the tube of mercury and floats to the surface because the mercury is so dense. A portion of the liquid evaporates at the top of the column, producing a vapor whose pressure pushes some mercury out of the tube. When the system reaches equilibrium, the vapor pressure can be determined from the change in the height of the mercury column since

$$P_{\text{atmosphere}} = P_{\text{vapor}} + P_{\text{Hg column}}$$

Thus

$$P_{\text{vapor}} = P_{\text{atmosphere}} - P_{\text{Hg column}}$$

The vapor pressures of liquids vary widely [see Fig. 10.40(b)]. Liquids with high vapor pressures are said to be *volatile*—they evaporate rapidly from an open dish. The vapor pressure of a liquid is principally determined by the size of the *intermolecular forces* in the liquid. Liquids in which the intermolecular forces are large have relatively low vapor pressures because the molecules need high energies to escape to the vapor phase. For example, although water has a much lower molar mass than diethyl ether, the strong hydrogen-bonding forces that exist among wa-

FIGURE 10.39

The rates of condensation and evaporation over time for a liquid sealed in a closed container. The rate of evaporation remains constant and the rate of condensation increases as the number of molecules in the vapor phase increases, until the two rates become equal. At this point, the equilibrium vapor pressure is attained.

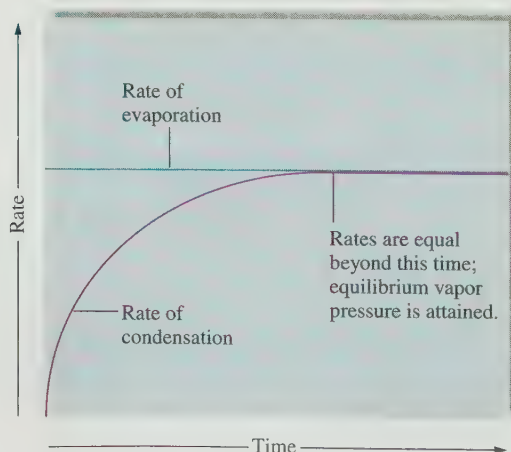
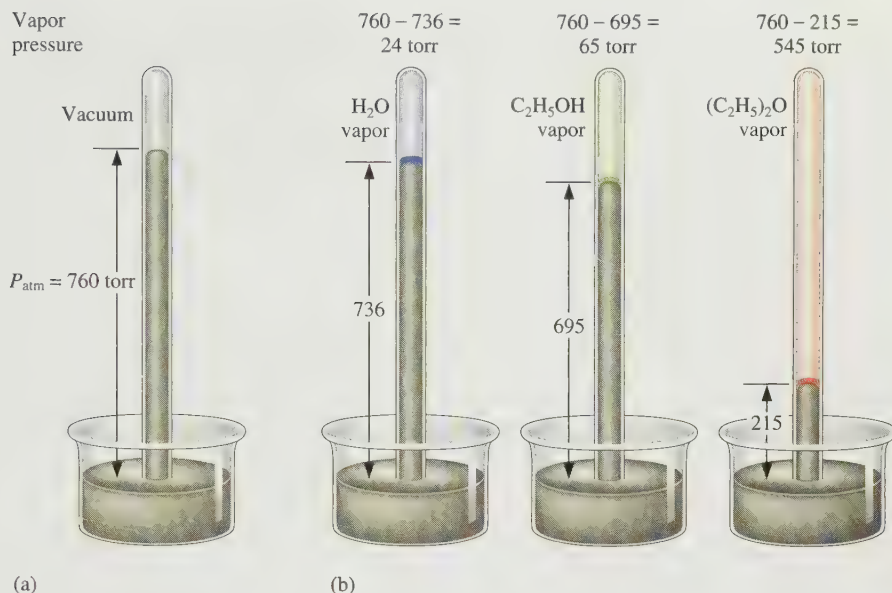


FIGURE 10.40

(a) The vapor pressure of a liquid can be measured easily using a simple barometer of the type shown here. (b) The three liquids, water, ethanol ($\text{C}_2\text{H}_5\text{OH}$), and diethyl ether [$(\text{C}_2\text{H}_5)_2\text{O}$], have quite different vapor pressures. Ether is by far the most volatile of the three. Note that in each case a little liquid remains (floating on the mercury).



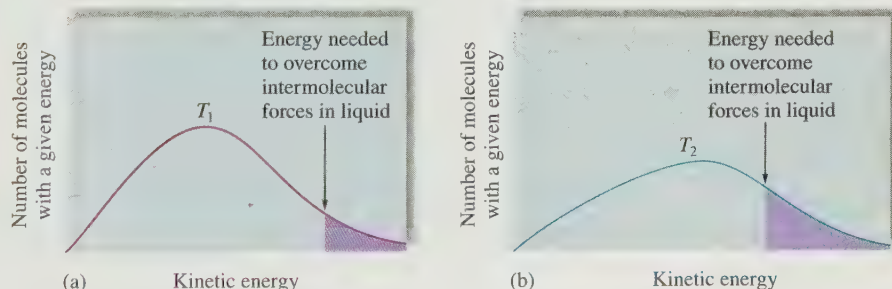
ter molecules in the liquid cause water's vapor pressure to be much lower than that of diethyl ether [see Fig. 10.40(b)]. In general, substances with large molar masses have relatively low vapor pressures, mainly because of the large dispersion forces. The more electrons a substance has, the more polarizable it is, and the greater are the dispersion forces.

Measurements of the vapor pressure for a given liquid at several temperatures show that *vapor pressure increases significantly with temperature*. Figure 10.41 illustrates the distribution of molecular kinetic energy present in a liquid at two different temperatures. To overcome the intermolecular forces in a liquid, a molecule must have sufficient kinetic energy. As the temperature of the liquid is increased, the fraction of molecules having the minimum energy needed to overcome these forces and escape to the vapor phase increases markedly. Thus the vapor pressure of a liquid increases dramatically with temperature. Values for water at several temperatures are given in Table 10.8.

TABLE 10.8

The Vapor Pressure of Water as a Function of Temperature

T ($^{\circ}\text{C}$)	P (torr)
0.0	4.579
10.0	9.209
20.0	17.535
25.0	23.756
30.0	31.824
40.0	55.324
60.0	149.4
70.0	233.7
90.0	525.8

**FIGURE 10.41**

The number of molecules in a liquid with a given energy versus kinetic energy at two temperatures. Part (a) shows a lower temperature than that in part (b). Note that the proportion of molecules with enough energy to escape the liquid to the vapor phase (indicated by shaded areas) increases dramatically with temperature. This causes vapor pressure to increase markedly with temperature.

The quantitative nature of the temperature dependence of vapor pressure can be represented graphically. Plots of vapor pressure versus temperature for water, ethanol, and diethyl ether are shown in Fig. 10.42(a). Note the nonlinear increase in vapor pressure for all the liquids as the temperature is increased. We find that a straight line can be obtained by plotting $\ln(P_{\text{vap}})$ versus $1/T$, where T is the Kelvin temperature, as shown in Fig. 10.42(b). We can represent this behavior by the equation

$$\ln(P_{\text{vap}}) = -\frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T} \right) + C \quad (10.4)$$

where ΔH_{vap} is the enthalpy of vaporization, R is the universal gas constant, and C is a constant characteristic of a given liquid. The symbol $\ln$ means that the natural logarithm of the vapor pressure is taken.

Equation (10.4) is the equation for a straight line of the form $y = mx + b$, where

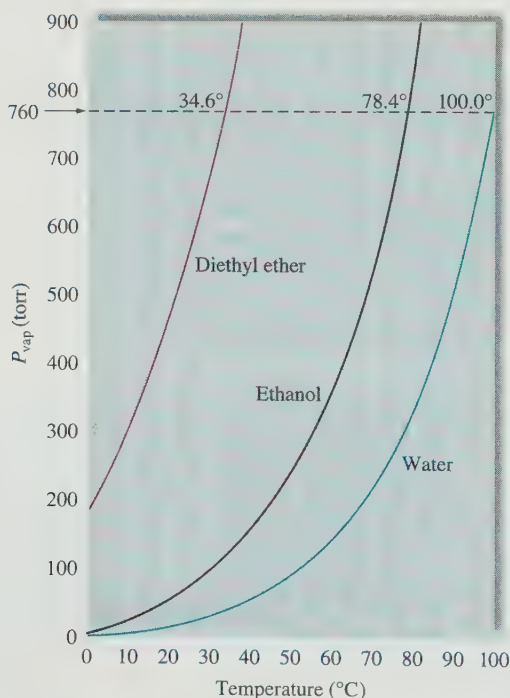
$$y = \ln(P_{\text{vap}})$$

$$x = \frac{1}{T}$$

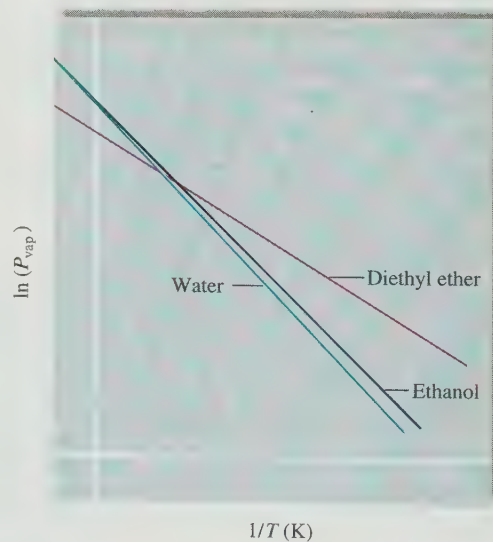
$$m = \text{slope} = -\frac{\Delta H_{\text{vap}}}{R}$$

$$b = \text{intercept} = C$$

Natural logarithms are reviewed in Appendix 1.2.



(a)



(b)

FIGURE 10.42

(a) The vapor pressure of water, ethanol, and diethyl ether as a function of temperature. (b) Plots of $\ln(P_{\text{vap}})$ versus $1/T$ (Kelvin temperature) for water, ethanol, and diethyl ether.

SAMPLE EXERCISE 10.5

Determining Enthalpies of Vaporization

Using the plots in Fig. 10.42(b), determine whether water or diethyl ether has the larger enthalpy of vaporization.

SOLUTION

When $\ln(P_{\text{vap}})$ is plotted versus $1/T$, the slope of the resulting straight line is

$$-\frac{\Delta H_{\text{vap}}}{R}$$

Note from Fig. 10.42(b) that the slopes of the lines for water and diethyl ether are both negative, as expected, and that the line for ether has the smaller slope. Thus ether has the smaller value of ΔH_{vap} . This makes sense because the hydrogen bonding in water causes it to have a relatively large enthalpy of vaporization.

See Exercise 10.75.

Equation (10.4) is important for several reasons. For example, we can determine the heat of vaporization for a liquid by measuring P_{vap} at several temperatures and then evaluating the slope of a plot of $\ln(P_{\text{vap}})$ versus $1/T$. On the other hand, if we know the values of ΔH_{vap} and P_{vap} at one temperature, we can use Equation (10.4) to calculate P_{vap} at another temperature. This can be done by recognizing that the constant C does not depend on temperature. Thus at two temperatures T_1 and T_2 we can solve Equation (10.4) for C and then write the equality

$$\ln(P_{\text{vap},T_1}) + \frac{\Delta H_{\text{vap}}}{RT_1} = C = \ln(P_{\text{vap},T_2}) + \frac{\Delta H_{\text{vap}}}{RT_2}$$

This can be rearranged to

$$\ln(P_{\text{vap},T_1}) - \ln(P_{\text{vap},T_2}) = \frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

or

$$\ln\left(\frac{P_{\text{vap},T_1}}{P_{\text{vap},T_2}}\right) = \frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (10.5)$$

Equation 10.5 is called the *Clausius–Clapeyron equation*.

SAMPLE EXERCISE 10.6

Calculating Vapor Pressure

The vapor pressure of water at 25°C is 23.8 torr, and the heat of vaporization of water at 25°C is 43.9 kJ/mol. Calculate the vapor pressure of water at 50.°C.

SOLUTION

We will use Equation (10.5):

$$\ln\left(\frac{P_{\text{vap},T_1}}{P_{\text{vap},T_2}}\right) = \frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

For water we have

$$P_{\text{vap},T_1} = 23.8 \text{ torr}$$

$$T_1 = 25 + 273 = 298 \text{ K}$$

$$T_2 = 50. + 273 = 323 \text{ K}$$

$$\Delta H_{\text{vap}} = 43.9 \text{ kJ/mol} = 43,900 \text{ J/mol}$$

$$R = 8.3145 \text{ J/K mol}$$

In solving this problem, we ignore the fact that ΔH_{vap} is slightly temperature dependent.

$$\begin{aligned}\text{Thus} \quad \ln\left(\frac{23.8 \text{ torr}}{P_{\text{vap},T_2} \text{ (torr)}}\right) &= \frac{43,900 \text{ J/mol}}{8.3145 \text{ J/K mol}} \left(\frac{1}{323 \text{ K}} - \frac{1}{298 \text{ K}}\right) \\ \ln\left(\frac{23.8}{P_{\text{vap},T_2}}\right) &= -1.37\end{aligned}$$

Phase changes of carbon dioxide are discussed in Section 10.9.

Taking the antilog (see Appendix 1.2) of both sides gives

$$\begin{aligned}\frac{23.8}{P_{\text{vap},T_2}} &= 0.254 \\ P_{\text{vap},T_2} &= 93.7 \text{ torr}\end{aligned}$$

See Exercises 10.77 through 10.80.

Sublimation: A process in which a substance goes directly from the solid to the gaseous state.

Like liquids, solids have vapor pressures. Figure 10.43 shows iodine vapor in equilibrium with solid iodine in a closed flask. Under normal conditions iodine **sublimes**; that is, it goes directly from the solid to the gaseous state without passing through the liquid state. **Sublimation** also occurs with dry ice (solid carbon dioxide).

Changes of State



Understanding Concepts: Changes of State

What happens when a solid is heated? Typically, it will melt to form a liquid. If the heating continues, the liquid will at some point boil and form the vapor phase. This process can be represented by a **heating curve**: a plot of temperature versus time for a process where energy is added at a constant rate.

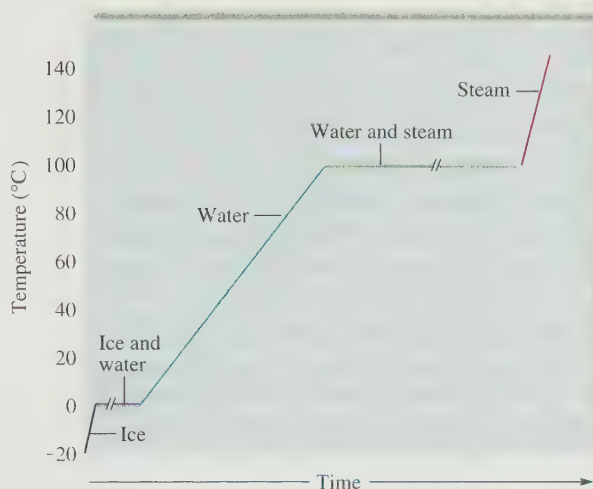
The heating curve for water is given in Fig. 10.44. As energy flows into the ice, the random vibrations of the water molecules increase as the temperature rises. Eventually, the molecules become so energetic that they break loose from their lattice



FIGURE 10.43
Iodine being heated, causing it to sublime onto an evaporating dish cooled by ice.

FIGURE 10.44

The heating curve (not drawn to scale) for a given quantity of water where energy is added at a constant rate. The plateau at the boiling point is longer than the plateau at the melting point because it takes almost seven times more energy (and thus seven times the heating time) to vaporize liquid water than to melt ice. The slopes of the other lines are different because the different states of water have different molar heat capacities (the energy required to raise the temperature of 1 mole of a substance by 1°C).



Ionic solids such as NaCl and NaF have very high melting points and enthalpies of fusion because of the strong ionic forces in these solids. At the other extreme is $O_2(s)$, a molecular solid containing nonpolar molecules with weak intermolecular forces. (See Table 10.9.)

The melting and boiling points will be defined more precisely later in this section.

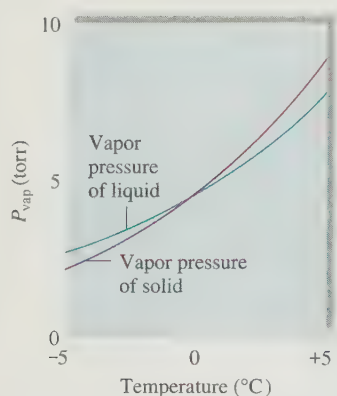
positions, and the change from solid to liquid occurs. This is indicated by a plateau at 0°C on the heating curve. At this temperature, called the *melting point*, all the added energy is used to disrupt the ice structure by breaking the hydrogen bonds, thus increasing the potential energy of the water molecules. The enthalpy change that occurs at the melting point when a solid melts is called the **heat of fusion**, or more accurately, the **enthalpy of fusion**, ΔH_{fus} . The melting points and enthalpies of fusion for several representative solids are listed in Table 10.9.

The temperature remains constant until the solid has completely changed to liquid; then it begins to increase again. At 100°C the liquid water reaches its *boiling point*, and the temperature then remains constant as the added energy is used to vaporize the liquid. When the liquid is completely changed to vapor, the temperature again begins to rise. Note that changes of state are physical changes; although intermolecular forces have been overcome, no chemical bonds have been broken. If the water vapor were heated to much higher temperatures, the water molecules would break down into the individual atoms. This would be a chemical change, since covalent bonds are broken. We no longer have water after this occurs.

The melting and boiling points for a substance are determined by the vapor pressures of the solid and liquid states. Figure 10.45 shows the vapor pressures of

TABLE 10.9 Melting Points and Enthalpies of Fusion for Several Representative Solids

Compound	Melting Point (°C)	Enthalpy of Fusion (kJ/mol)
O_2	-218	0.45
HCl	-114	1.99
HI	-51	2.87
CCl_4	-23	2.51
$CHCl_3$	-64	9.20
H_2O	0	6.02
NaF	992	29.3
NaCl	801	30.2

**FIGURE 10.45**

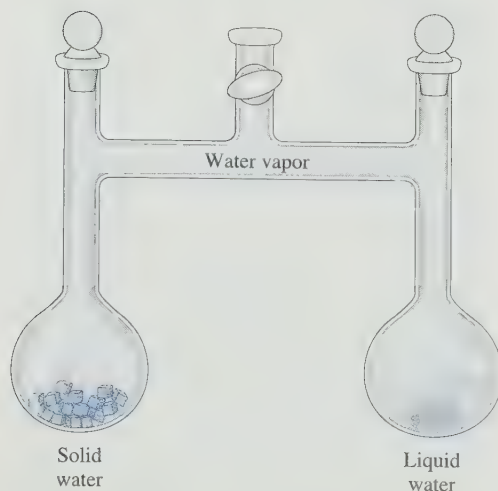
The vapor pressures of solid and liquid water as a function of temperature. The data for liquid water below 0°C are obtained from super-cooled water. The data for solid water above 0°C are estimated by extrapolation of vapor pressure from below 0°C.

solid and liquid water as functions of temperature near 0°C. Note that below 0°C the vapor pressure of ice is less than the vapor pressure of liquid water. Also note that the vapor pressure of ice has a larger temperature dependence than that of the liquid. That is, the vapor pressure of ice increases more rapidly for a given rise in temperature than does the vapor pressure of water. Thus, as the temperature of the solid is increased, a point is eventually reached where the *liquid and solid have identical vapor pressures*. This is the melting point.

These concepts can be demonstrated experimentally using the apparatus illustrated in Fig. 10.46, where ice occupies one compartment and liquid water the other. Consider the following cases.

Case 1. A temperature at which the vapor pressure of the solid is greater than that of the liquid. At this temperature the solid requires a higher pressure than the liquid does to be in equilibrium with the vapor. Thus, as vapor is released from the solid to try to achieve equilibrium, the liquid will absorb vapor in an attempt to reduce the vapor pressure to its equilibrium value. The net effect is a conversion from solid to liquid through the vapor phase. In fact, no solid can exist under these conditions. The amount of solid will steadily decrease and the volume of liquid will increase. Finally, there will be only liquid in the right compartment, which will come to equilibrium with the water vapor, and no further changes will occur in the system. This temperature must be above the melting point of ice, since only the liquid state can exist.

Case 2. A temperature at which the vapor pressure of the solid is less than that of the liquid. This is the opposite of the situation in case 1. In this case, the liquid requires a higher pressure than the solid does to be in equilibrium with the vapor, so the liquid will gradually disappear, and the amount of ice will increase. Finally, only the solid will remain, which will achieve equilibrium with the vapor. This temperature must be *below the melting point* of ice, since only the solid state can exist.

**FIGURE 10.46**

An apparatus that allows solid and liquid water to interact only through the vapor state.

Constant pressure
of 1 atmosphere

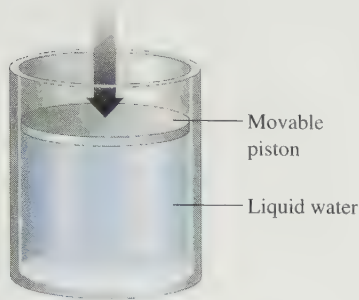


FIGURE 10.47

Water in a closed system with a pressure of 1 atm exerted on the piston. No bubbles can form within the liquid as long as the vapor pressure is less than 1 atm.

Case 3. A temperature at which the vapor pressures of the solid and liquid are identical. In this case, the solid and liquid states have the same vapor pressure, so they can coexist in the apparatus at equilibrium simultaneously with the vapor. This temperature represents the *freezing point* where both the solid and liquid states can exist.

We can now describe the melting point of a substance more precisely. The **normal melting point** is defined as *the temperature at which the solid and liquid states have the same vapor pressure under conditions where the total pressure is 1 atmosphere*.

Boiling occurs when the vapor pressure of a liquid becomes equal to the pressure of its environment. The **normal boiling point** of a liquid is *the temperature at which the vapor pressure of the liquid is exactly 1 atmosphere*. This concept is illustrated in Fig. 10.47. At temperatures where the vapor pressure of the liquid is less than 1 atmosphere, no bubbles of vapor can form because the pressure on the surface of the liquid is greater than the pressure in any spaces in the liquid where the bubbles are trying to form. Only when the liquid reaches a temperature at which the pressure of vapor in the spaces in the liquid is 1 atmosphere can bubbles form and boiling occur.

However, changes of state do not always occur exactly at the boiling point or melting point. For example, water can be readily **supercooled**; that is, it can be cooled below 0°C at 1 atm pressure and remain in the liquid state. Supercooling occurs because, as it is cooled, the water may not achieve the degree of organization necessary to form ice at 0°C , and thus it continues to exist as the liquid. At some point the correct ordering occurs and ice rapidly forms, releasing energy in the exothermic process and bringing the temperature back up to the melting point, where the remainder of the water freezes (see Fig. 10.48).

A liquid also can be **superheated**, or raised to temperatures above its boiling point, especially if it is heated rapidly. Superheating can occur because bubble formation in the interior of the liquid requires that many high-energy molecules gather



Boiling chip releasing air bubbles acts as a nucleating agent for the bubbles that form when water boils.

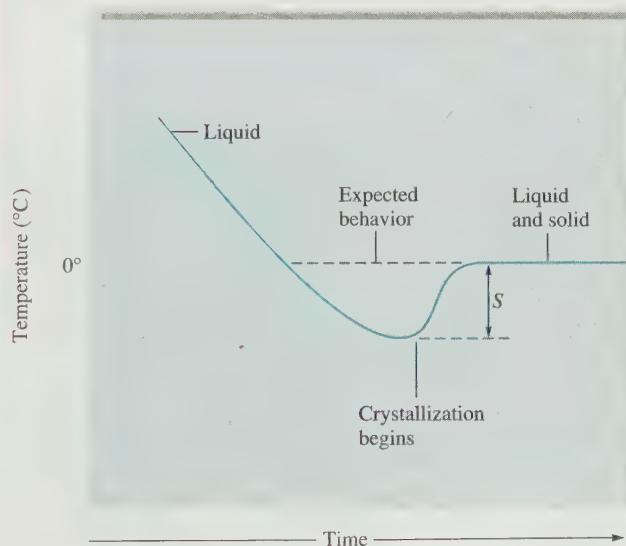


FIGURE 10.48

The supercooling of water. The extent of supercooling is given by S.

in the same vicinity, and this may not happen at the boiling point, especially if the liquid is heated rapidly. If the liquid becomes superheated, the vapor pressure in the liquid is greater than the atmospheric pressure. Once a bubble does form, since its internal pressure is greater than that of the atmosphere, it can burst before rising to the surface, blowing the surrounding liquid out of the container. This is called *bumping* and has ruined many experiments. It can be avoided by adding boiling chips to the flask containing the liquid. Boiling chips are bits of porous ceramic material containing trapped air that escapes on heating, forming tiny bubbles that act as “starters” for vapor bubble formation. This allows a smooth onset of boiling as the boiling point is reached.

10.9 Phase Diagrams

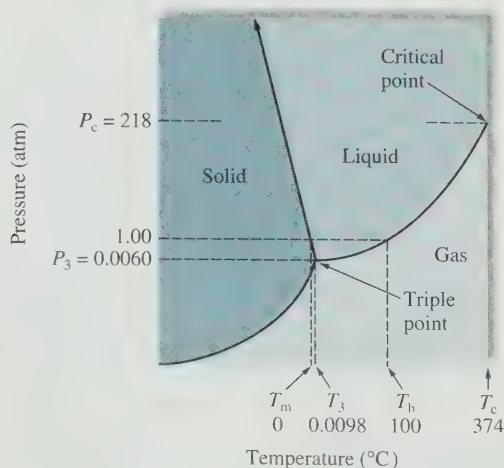
A **phase diagram** is a convenient way of representing the phases of a substance as a function of temperature and pressure. For example, the phase diagram for water (Fig. 10.49) shows which state exists at a given temperature and pressure. It is important to recognize that a phase diagram describes conditions and events in a *closed* system of the type represented in Fig. 10.47, where no material can escape into the surroundings and no air is present. Notice that the diagram is not drawn to scale (neither axis is linear). This is done to emphasize certain features of the diagram that will be discussed below.

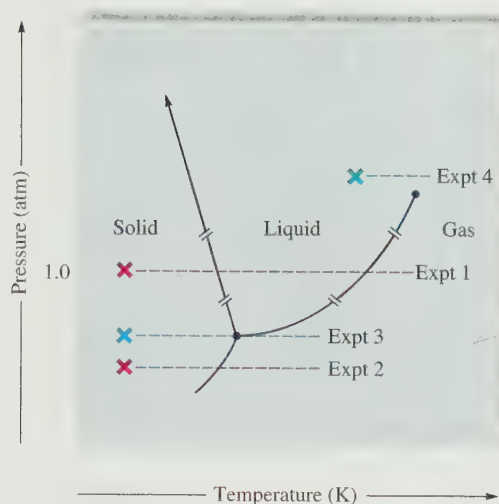
To show how to interpret the phase diagram for water, we will consider heating experiments at several pressures, shown by the dashed lines in Fig. 10.50.

Experiment 1. *Pressure is 1 atm.* This experiment begins with the cylinder shown in Fig. 10.47 completely filled with ice at a temperature of -20°C and the piston exerting a pressure of 1 atm directly on the ice (there is no air space). Since at temperatures below 0°C the vapor pressure of ice is less than 1 atm—which is the constant external pressure on the piston—no vapor is present in the cylinder. As the cylinder is heated, ice is the only component until the temperature reaches 0°C , where the ice changes to liquid water as energy is added. This is the normal melt-

FIGURE 10.49

The phase diagram for water. T_m represents the normal melting point; T_3 and P_3 denote the triple point; T_b represents the normal boiling point; T_c represents the critical temperature; P_c represents the critical pressure. The negative slope of the solid/liquid line reflects the fact that the density of ice is less than that of liquid water. (Note that this line extends indefinitely, as indicated by the arrow.)



**FIGURE 10.50**

Diagrams of various heating experiments on samples of water in a closed system.

ing point of water. Note that under these conditions no vapor exists in the system. The vapor pressures of the solid and liquid are equal, but this vapor pressure is less than 1 atm, so no water vapor can exist. This is true on the solid/liquid line everywhere except at the triple point (see Experiment 3 below). When the solid has completely changed to liquid, the temperature again rises. At this point, the cylinder contains only liquid water. *No vapor is present* because the vapor pressure of liquid water under these conditions is less than 1 atm, the constant external pressure on the piston. Heating continues until the temperature of the liquid water reaches 100°C. At this point, the vapor pressure of liquid water is 1 atm, and boiling occurs, with the liquid changing to vapor. This is the normal boiling point of water. After the liquid has been completely converted to steam, the temperature again rises as the heating continues. The cylinder now contains only water vapor.

Experiment 2. *Pressure is 2.0 torr.* Again, we start with ice as the only component in the cylinder at -20°C . The pressure exerted by the piston in this case is only 2.0 torr. As heating proceeds, the temperature rises to -10°C , where the ice changes directly to vapor, a process known as *sublimation*. Sublimation occurs when the vapor pressure of ice is equal to the external pressure, which in this case is only 2.0 torr. No liquid water appears under these conditions because the vapor pressure of liquid water is always greater than 2.0 torr, and thus it cannot exist at this pressure. If liquid water were placed in a cylinder under such a low pressure, it would vaporize immediately at temperatures above -10°C or freeze at temperatures below -10°C .

Experiment 3. *Pressure is 4.58 torr.* Again, we start with ice as the only component in the cylinder at -20°C . In this case the pressure exerted on the ice by the piston is 4.58 torr. As the cylinder is heated, no new phase appears until the temperature reaches 0.01°C (273.16 K). At this point, called the **triple point**, solid and liquid water have identical vapor pressures of 4.58 torr. Thus at 0.01°C (273.16 K) and

4.58 torr all three states of water are present. In fact, only under these conditions can all three states of water coexist in a closed system.

Experiment 4. *Pressure is 225 atm.* In this experiment we start with liquid water in the cylinder at 300°C; the pressure exerted by the piston on the water is 225 atm. Liquid water can be present at this temperature because of the high external pressure. As the temperature increases, something happens that we did not see in the first three experiments: the liquid gradually changes into a vapor but goes through an intermediate “fluid” region, which is neither true liquid nor vapor. This is quite unlike the behavior at lower temperatures and pressures, say at 100°C and 1 atm, where the temperature remains constant while a definite phase change from liquid to vapor occurs. This unusual behavior occurs because the conditions are beyond the critical point for water. The **critical temperature** can be defined as the temperature above which the vapor cannot be liquefied no matter what pressure is applied. The **critical pressure** is the pressure required to produce liquefaction at the critical temperature. Together, the critical temperature and the critical pressure define the **critical point**. For water the critical point is 374°C and 218 atm. Note that the liquid/vapor line on the phase diagram for water ends at the critical point. Beyond this point the transition from one state to another involves the intermediate “fluid” region just described.

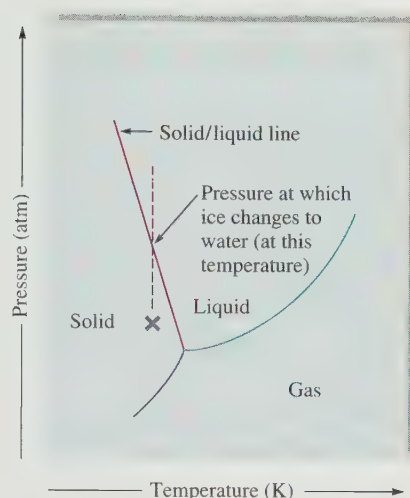
Applications of the Phase Diagram for Water

There are several additional interesting features of the phase diagram for water. Note that the solid/liquid boundary line has a negative slope. This means that the melting point of ice *decreases* as the external pressure *increases*. This behavior, which is opposite to that observed for most substances, occurs because the density of ice is *less* than that of liquid water at the melting point. The maximum density of water occurs at 4°C; when liquid water freezes, its volume increases.

We can account for the effect of pressure on the melting point of water using the following reasoning. At the melting point, liquid and solid water coexist—they are in dynamic equilibrium, since the rate at which ice is melting is just balanced by the rate at which the water is freezing. What happens if we apply pressure to this system? When subjected to increased pressure, matter reduces its volume. This behavior is most dramatic for gases but also occurs for condensed states. Since a given mass of ice at 0°C has a larger volume than the same mass of liquid water, the system can reduce its volume in response to the increased pressure by changing to liquid. Thus at 0°C and an external pressure greater than 1 atm, water is liquid. In other words, the freezing point of water is less than 0°C when the pressure is greater than 1 atm.

Figure 10.51 illustrates the effect of pressure on ice. At the point X on the phase diagram, ice is subjected to increased pressure at constant temperature. Note that as the pressure is increased, the solid/liquid line is crossed, indicating that the ice melts. This phenomenon may be important in ice skating. The narrow blade of the skate exerts a large pressure, since the skater’s weight is supported by the small area of the blade. Also, the frictional heating due to the moving skate contributes to the melting of the ice.* After the blade passes, the liquid refreezes as normal pressure

* The physics of ice skating is quite complex, and there is disagreement about whether the pressure or the frictional heating of the ice skate is most important. See “Letter to the Editor,” by R. Silberman, *J. Chem. Ed.* **65** (1988): 186.

**FIGURE 10.51**

The phase diagram for water. At point X on the phase diagram, water is a solid. However, as the external pressure is increased while the temperature remains constant (indicated by the vertical dotted line), the solid/liquid line is crossed and the ice melts.



The effect of pressure on ice allows this skater to glide smoothly.

and temperature return. Without this lubrication effect due to the thawing ice, ice skating would not be the smooth, graceful activity that many people enjoy.

Ice's lower density has other implications. When water freezes in a pipe or an engine block, it will expand and break the container. This is why water pipes are insulated in cold climates and antifreeze is used in water-cooled engines. The lower density of ice also means that ice formed on rivers and lakes will float, providing a layer of insulation that helps prevent bodies of water from freezing solid in the winter. Aquatic life can therefore continue to live through periods of freezing temperatures.

A liquid boils at the temperature where the vapor pressure of the liquid equals the external pressure. Thus the boiling point of a substance, like the melting point, depends on the external pressure. This is why water boils at different temperatures at different elevations (see Table 10.10), and any cooking carried out in boiling

TABLE 10.10 Boiling Point of Water at Various Locations

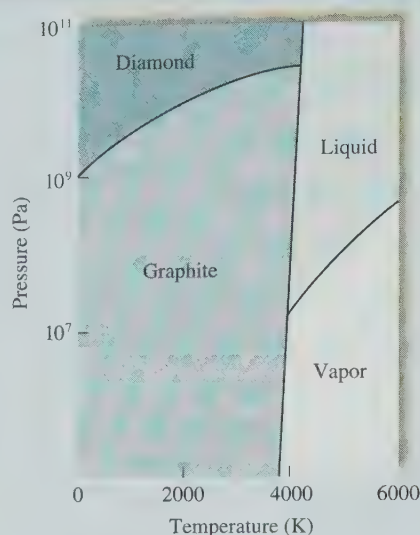
Location	Feet Above Sea Level	P_{atm} (torr)	Boiling Point ($^{\circ}\text{C}$)
Top of Mt. Everest, Tibet	29,028	240	70
Top of Mt. McKinley, Alaska	20,320	340	79
Top of Mt. Whitney, Calif.	14,494	430	85
Leadville, Colo.	10,150	510	89
Top of Mt. Washington, N.H.	6,293	590	93
Boulder, Colo.	5,430	610	94
Madison, Wis.	900	730	99
New York City, N.Y.	10	760	100
Death Valley, Calif.	-282	770	100.3

Making Diamonds at Low Pressures: Fooling Mother Nature

In 1955 Robert H. Wentorf, Jr., accomplished something that borders on alchemy—he turned peanut butter into diamonds. He and his coworkers at the General Electric Research and Development Center also changed roofing pitch, wood, coal, and many other carbon-containing materials into diamonds, using a process involving temperatures of $\approx 2000^\circ\text{C}$ and pressures of $\approx 10^5$ atm. Although the first diamonds made by this process looked like black sand because of the impurities present, the process has now been developed to a point such that beautiful, clear, gem-quality diamonds can be produced. General Electric now has the capacity to produce 150 million carats (30,000 kg) of diamonds annually (virtually all of which is “diamond grit” used for industrial purposes such as abrasive coatings on cutting tools). The production of large, gem-quality diamonds by this process is still too expensive to compete with the natural sources of these stones. However, this may change as methods are developed for making diamonds at low pressures.

The high temperatures and pressures used in the GE process for making diamonds make sense if one looks at the accompanying phase diagram for carbon. Note that graphite—not diamond—is the most stable form of carbon under ordinary conditions of temperature and pressure. However, diamond becomes more stable than graphite at very high pressures (as one would expect from the greater density of diamond). The high temperature used in the GE process is necessary to disrupt the bonds in graphite so that diamond (the most stable form of carbon at the high pressures used in the process) can form. Once the diamond is produced, the elemental carbon is “trapped” in this form at normal conditions (25°C , 1 atm) because the reaction back to the graphite form is so slow. That is, even though graphite is more stable than diamond at 25°C and 1 atm, diamond can exist almost indefinitely because the conversion to graphite is a very *slow* reaction. As a result, diamonds formed at the high pressures found deep in the earth’s crust can be brought to the earth’s surface by natural geologic processes and continue to exist for millions of years.*

We have seen that diamond formed in the laboratory at high pressures is “trapped” in this form, but this process is very expensive. Can diamond be formed at low pressures? The phase diagram for carbon says no. However, researchers have found that under the right conditions diamonds can be “grown” at low pressures. The process used is called *chemical vapor deposition* (CVD). CVD uses an energy source to release carbon atoms from a compound such as methane into a steady flow of hydrogen gas (some of which is dissociated to produce hydrogen atoms). The carbon atoms then deposit as a di-



The phase diagram for carbon.

amond film on a surface maintained at a temperature between 600 and 900°C . Why does diamond form on this surface rather than the favored graphite? Nobody is sure, but it has been suggested that at these relatively high temperatures the diamond structure grows faster than the graphite structure and so diamond is favored under these conditions. It also has been suggested that the hydrogen atoms present react much faster with graphite fragments than with diamond fragments, effectively removing any graphite from the growing film. Once it forms, of course, diamond is trapped. The major advantage of CVD is that there is no need for the extraordinarily high pressures used in the traditional process for synthesizing diamonds.

The first products with diamond films are already on the market. Audiophiles can buy tweeters that have diaphragms coated with a thin diamond film that limits sound distortion. Watches with diamond-coated crystals are planned, as are diamond-coated windows in infrared scanning devices used in analytical instruments and missile guidance systems. These applications represent only the beginning for diamond-coated products.

*In Morocco, a 50-km-long slab called Beni Bousera contains chunks of graphite that were probably once diamonds formed in the deposit when it was buried 150 km underground. As this slab slowly rose to the surface over millions of years, the very slow reaction changing diamond to graphite had time to occur. On the other hand, in the diamond-rich kimberlite deposits in South Africa, which rise to the surface much faster, the diamonds have not had sufficient time to revert to graphite.

Water boils at 89°C in Leadville, Colorado.

water will be affected by this variation. For example, it takes longer to hard-boil an egg in Leadville, Colorado (elevation: 10,150 ft), than in San Diego, California (sea level), since water boils at a lower temperature in Leadville.

As we mentioned earlier, the phase diagram for water describes a closed system. Therefore, we must be very cautious in using the phase diagram to explain the behavior of water in a natural setting, such as on the earth's surface. For example, in dry climates (low humidity), snow and ice seem to sublime—a minimum amount of slush is produced. Wet clothes put on an outside line at temperatures below 0°C freeze and then dry while frozen. However, the phase diagram (Fig. 10.47) shows that ice should *not* be able to sublime at normal atmospheric pressures. What is happening in these cases? Ice in the natural environment is not in a closed system. The pressure is provided by the atmosphere rather than by a solid piston. This means that the vapor produced over the ice can escape from the immediate region as soon as it is formed. The vapor does not come to equilibrium with the solid, and the ice slowly disappears. Sublimation, which seems forbidden by the phase diagram, does in fact occur under these conditions, although it is not the sublimation under equilibrium conditions described by the phase diagram.

The Phase Diagram for Carbon Dioxide

The phase diagram for carbon dioxide (Fig. 10.52) differs from that for water. The solid/liquid line has a positive slope, since solid carbon dioxide is more dense than liquid carbon dioxide. The triple point for carbon dioxide occurs at 5.1 atm and -56.6°C , and the critical point occurs at 72.8 atm and 31°C . At a pressure of 1 atm, solid carbon dioxide sublimates at -78°C , a property that leads to its common name, *dry ice*. No liquid phase occurs under normal atmospheric conditions, making dry ice a convenient refrigerant.

Carbon dioxide is often used in fire extinguishers, where it exists as a liquid at 25°C under high pressures. Liquid carbon dioxide released from the extinguisher into the environment at 1 atm immediately changes to a vapor. Being heavier than air, this vapor smothers the fire by keeping oxygen away from the flame. The liquid/vapor transition is highly endothermic, so cooling also results, which helps to put out the fire.



A carbon dioxide fire extinguisher.

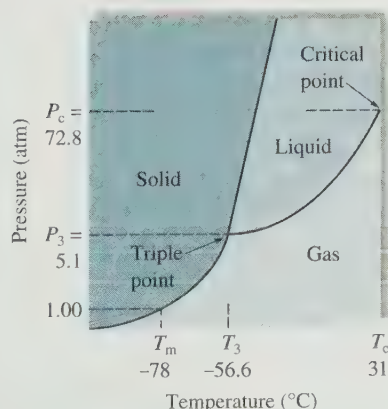


FIGURE 10.52

The phase diagram for carbon dioxide. The liquid state does not exist at a pressure of 1 atm. The solid/liquid line has a positive slope, since the density of solid carbon dioxide is greater than that of liquid carbon dioxide.

For Review

Summary

Key Terms

Section 10.1

condensed states
intermolecular forces
dipole–dipole attraction
hydrogen bonding
London dispersion forces

Section 10.2

surface tension
capillary action
viscosity

Section 10.3

crystalline solid
amorphous solid
lattice
unit cell
X-ray diffraction
ionic solid
molecular solid
atomic solid

Section 10.4

closest packing
hexagonal closest packed (hcp)
structure
cubic closest packed (ccp) structure
band model
molecular orbital (MO) model
alloy
substitutional alloy
interstitial alloy

Section 10.5

network solid
silica
silicate
glass
ceramic
semiconductor
n-type semiconductor
p-type semiconductor
p–n junction

Section 10.8

vaporization (evaporation)
heat of vaporization
enthalpy of vaporization (ΔH_{vap})
condensation
equilibrium

Liquids and solids are the two condensed states of matter; their formation is caused by intermolecular forces among the molecules, atoms, or ions. Dipole–dipole forces are attractions between molecules that have dipole moments. These forces are particularly strong for molecules containing hydrogen bonded to a highly electronegative element such as nitrogen, oxygen, or fluorine. In these cases the resulting dipole forces are called hydrogen bonds and account for the unusually high boiling points of the hydrides of the first elements in Groups 5A, 6A, and 7A. London dispersion forces caused by instantaneous dipoles are important in substances composed of nonpolar molecules. Liquids exhibit various properties—surface tension, capillary action, and viscosity—that depend on the strengths of the intermolecular forces.

The two broadest categories of solids are crystalline and amorphous solids. Crystalline solids have a regular arrangement, or lattice, of component particles, the smallest repeating unit of which is the unit cell. Crystalline solids can be classified according to what type of components occupy the lattice points: atoms (atomic solids), ions (ionic solids), or molecules (molecular solids). The arrangement of particles in a crystalline solid can be determined by X-ray diffraction techniques, and the interatomic distances in the crystal can be related to the wavelength and angle of reflection of the X rays by the Bragg equation.

The structure of metals is modeled by assuming atoms to be uniform spheres and packing them as compactly as possible. There are two closest packing arrangements: hexagonal and cubic.

The bonding in metallic crystals can be described in terms of the electron sea model (valence electrons are assumed to move freely about the metal cations) or in terms of the band model (electrons are assumed to travel through the metal crystal in molecular orbitals formed from the valence atomic orbitals of the metal atoms). In the band model the large number of available atomic orbitals form closely spaced energy levels. Electricity can be readily conducted by electrons in conduction bands, which are molecular orbitals containing only a single electron.

Metals form alloys, which can be classified as substitutional or interstitial.

Carbon is a typical network solid containing strong directional covalent bonds. Diamond and graphite are two allotropes of carbon, with very different physical properties determined by their different bonding.

Silicon should be very similar in properties to carbon since carbon and silicon are next to each other in Group 4A, but in fact their compounds are markedly dissimilar. Silica, the fundamental silicon–oxygen compound, does not contain discrete SiO_2 molecules but rather a network of interconnected SiO_4 tetrahedra. Silicates, salts containing polyatomic anions of silicon and oxygen, are components of rocks, soil, clays, glass, and ceramics.

Semiconductors are formed when pure silicon is doped with other elements. An n-type semiconductor contains atoms with more valence electrons than the silicon atom, and a p-type semiconductor has atoms with fewer valence electrons than silicon. The modern electronics industry is based on devices with p–n junctions.

Molecular solids have small molecules at the lattice points and are held together by relatively weak intermolecular forces. Ice is an example. Ionic solids, on the other hand, are held together by strong electrostatic attractions. The crystal

equilibrium vapor pressure
sublimation
heating curve
enthalpy (heat) of fusion (ΔH_{fus})
normal melting point
normal boiling point
supercooled
superheated

Section 10.9

phase diagram
triple point
critical temperature
critical pressure
critical point

structure of ionic solids can often be described by fitting the smaller ions (usually cations) into holes in the closest packed structures formed by the larger ions (usually anions).

The phase change between liquid and vapor is called vaporization, or evaporation, and the energy required to change 1 mole of liquid to its vapor is the heat of vaporization (ΔH_{vap}). Condensation is the reverse process by which vapor molecules return to the liquid state. When the rates of evaporation and condensation exactly balance in a closed container, the system is at equilibrium, and the resulting pressure of the vapor is called the vapor pressure. The volatility of liquids depends on intermolecular forces. Liquids with strong intermolecular forces tend to have low vapor pressures.

The normal melting point of a solid is defined as the temperature at which the solid and its liquid have identical vapor pressures. The normal boiling point of a liquid occurs at a temperature where the vapor pressure of the liquid is 1 atmosphere.

A phase diagram for a substance shows which state exists at a given temperature and pressure. The triple point on a phase diagram represents the temperature and pressure where all three states coexist. The critical point is defined by the critical temperature and critical pressure. Critical temperature is that temperature above which the vapor cannot be liquefied no matter what pressure is applied. The critical pressure is the pressure required to produce liquefaction at the critical temperature.

In-Class Discussion Questions

These questions are designed to be considered by groups of students in class. Often these questions work well for introducing a particular topic in class.

1. It is possible to balance a paper clip on the surface of water in a beaker. If you add a bit of soap to the water, however, the paper clip sinks. Explain how the paper clip can float and why it sinks when soap is added.
2. Consider a sealed container half-filled with water. Which statement best describes what occurs in the container?
 - a. Water evaporates until the air is saturated with water vapor; at this point, no more water evaporates.
 - b. Water evaporates until the air is overly saturated (super-saturated) with water, and most of this water recondenses; this cycle continues until a certain amount of water vapor is present, and then the cycle ceases.
 - c. Water does not evaporate because the container is sealed.
 - d. Water evaporates, and then water evaporates and recondenses simultaneously and continuously.
 - e. Water evaporates until it is eventually all in vapor form. Explain each choice. Justify your choice, and for choices you did not pick, explain what is wrong with them.
3. Explain the following: You add 100 mL of water to a 500-mL round-bottom flask and heat the water until it is boiling. You remove the heat and stopper the flask, and the boiling stops. You then run cool water over the neck of the flask,

and the boiling begins again. It seems as though you are boiling water by cooling it.

4. Is it possible for the dispersion forces in a particular substance to be stronger than the hydrogen bonding forces in another substance? Explain your answer.
5. Does the nature of intermolecular forces change when a substance goes from a solid to a liquid, or from a liquid to a gas? What causes a substance to undergo a phase change?
6. Why do liquids have a vapor pressure? Do all liquids have vapor pressures? Explain. Do solids exhibit vapor pressure? Explain. How does vapor pressure change with changing temperature? Explain.
7. Water in an open beaker evaporates over time. As the water is evaporating, is the vapor pressure increasing, decreasing, or staying the same? Why?
8. What is the vapor pressure of water at 100°C? How do you know?
9. Refer to Fig. 10.44. Why doesn't temperature increase continuously over time? That is, why does the temperature stay constant for periods of time?
10. Which are stronger, intermolecular or intramolecular forces for a given molecule? What observation(s) have you made that support this? Explain.
11. Why does water evaporate?

A blue question or exercise number indicates that the answer to that question or exercise appears at the back of this book and a solution appears in the *Solutions Guide*.

Questions

12. What are dipole–dipole forces? How do typical dipole–dipole forces differ from hydrogen bonding interactions? In what ways are they similar? Describe the relationship between molecular size and the strength of London dispersion forces.
13. List the major types of intermolecular forces in order of increasing strength. Is there some overlap? That is, can the strongest London dispersion forces be greater than some dipole–dipole forces? Give an example of such an instance.
14. How do the following physical properties depend on the strength of intermolecular forces?
 - a. surface tension
 - b. viscosity
 - c. melting point
 - d. boiling point
 - e. vapor pressure
15. Distinguish between the following pairs.
 - a. polarizability and polarity
 - b. London dispersion forces and dipole–dipole forces
 - c. intermolecular forces and intramolecular forces
16. In what ways are liquids similar to solids? In what ways are liquids similar to gases?
17. Atoms are assumed to touch in closest packed structures, yet every closest packed unit cell contains a significant amount of empty space. Why?
18. Define *critical temperature* and *critical pressure*. In terms of the kinetic molecular theory, why is it impossible for a substance to exist as a liquid above its critical temperature?
19. What is the relationship between critical temperature and intermolecular forces?
20. Use the kinetic molecular theory to explain why a liquid gets cooler as it evaporates from an insulated container.
21. Distinguish between the items in the following pairs.
 - a. crystalline solid and amorphous solid
 - b. ionic solid and molecular solid
 - c. molecular solid and network solid
 - d. metallic solid and network solid
22. Will a crystalline solid or an amorphous solid give a simpler X-ray diffraction pattern? Why?
23. Use the band model to describe differences among insulators, conductors, and semiconductors. Also use the band model to explain why each of the following increases the conductivity of a semiconductor.
 - a. increasing the temperature
 - b. irradiating with light
 - c. adding an impurity
24. How do conductors and semiconductors differ as to the effect of temperature on electrical conductivity?
25. How can an n-type semiconductor be produced from pure germanium? How can a p-type semiconductor be produced from pure germanium?
26. What is an alloy? Explain the differences in structure between substitutional and interstitial alloys. Give an example of each type.
27. Define each of the following.
 - a. condensation
 - b. evaporation
 - c. sublimation
 - d. supercooled liquid
28. Describe what is meant by a dynamic equilibrium in terms of the vapor pressure of a liquid.
29. How does each of the following affect the rate of evaporation of a liquid in an open dish?
 - a. intermolecular forces
 - b. temperature
 - c. surface area
30. What do we mean when we say that a liquid is *volatile*? Do volatile liquids have large or small vapor pressures at room temperature? What strengths of intermolecular forces occur in highly volatile liquids?
31. When a person has a severe fever, one therapy used to reduce the fever is an “alcohol rub.” Explain how the evaporation of alcohol from a person’s skin removes heat energy from the body.
32. When wet laundry is hung on a clothesline on a cold winter day, it will freeze but eventually dry. Explain.
33. Why is a burn from steam typically much more severe than a burn from boiling water?
34. Why is the enthalpy of vaporization for water much greater than its enthalpy of fusion? What does this say about changes in intermolecular forces in going from solid to liquid to vapor?

Exercises

In this section similar exercises are paired.

Intermolecular Forces and Physical Properties

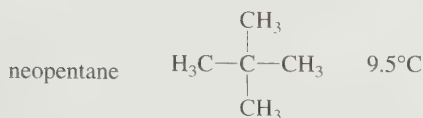
35. Identify the most important types of interparticle forces present in the solids of each of the following substances.
 - a. Ar
 - b. HCl
 - c. HF
 - d. CaCl_2
 - e. CH_4
 - f. CO
 - g. NaNO_3
36. Identify the most important types of interparticle forces present in the solids of each of the following substances.
 - a. NH_4Cl
 - b. Teflon, $\text{CF}_3(\text{CF}_2\text{CF}_2)_n\text{CF}_3$
 - c. Polyethylene, $\text{CH}_3(\text{CH}_2\text{CH}_2)_n\text{CH}_3$
 - d. CHCl_3
 - e. NH_3
 - f. NO
 - g. BF_3

37. Predict which substance in each of the following pairs would have the greater intermolecular forces.

- CO_2 or OCS
- SeO_2 or SO_2
- $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$ or $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$
- CH_3CH_3 or H_2CO
- CH_3OH or H_2CO

38. Rationalize the difference in boiling points for each of the following pairs of substances:

- n*-pentane $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ 36.2°C



- dimethyl ether CH_3OCH_3 -25°C
ethanol $\text{CH}_3\text{CH}_2\text{OH}$ 79°C
- HF 20°C
 HCl -85°C
- HCl -85°C
 LiCl 1360°C
- n*-pentane $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ 36.2°C
n-propane $\text{CH}_3\text{CH}_2\text{CH}_3$ -42°C
- n*-propane $\text{CH}_3\text{CH}_2\text{CH}_3$ -42°C
dimethyl ether CH_3OCH_3 -25°C

39. In each of the following groups of substances, pick the one that has the given property. Justify your answer.

- highest boiling point: HCl , Ar , or F_2
- highest freezing point: H_2O , NaCl , or HF
- lowest vapor pressure at 25°C : Cl_2 , Br_2 , or I_2
- lowest freezing point: N_2 , CO , or CO_2
- lowest boiling point: CH_4 , CH_3CH_3 , or $\text{CH}_3\text{CH}_2\text{CH}_3$
- highest boiling point: HF , HCl , or HBr

- lowest vapor pressure at 25°C : $\text{CH}_3\text{CH}_2\text{CH}_3$, CH_3CCH_3 , or $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$

40. In each of the following groups of substances, pick the one that has the given property. Justify each answer.

- highest boiling point: CCl_4 , CF_4 , or CBr_4
- lowest freezing point: LiF , Cl_2 , HBr
- smallest vapor pressure at 25°C : CH_3OCH_3 , $\text{CH}_3\text{CH}_2\text{OH}$, $\text{CH}_3\text{CH}_2\text{CH}_3$
- greatest viscosity: H_2S , HF , H_2O_2
- greatest heat of vaporization: H_2CO , CH_3CH_3 , CH_4
- smallest enthalpy of fusion: I_2 , CsBr , CaO

Properties of Liquids

41. The shape of the meniscus of water in a glass tube is different from that of mercury in a glass tube. Why?



H_2O in glass



Hg in glass

42. Explain why water forms into beads on a waxed car finish.

43. Hydrogen peroxide (H_2O_2) is a syrupy liquid with a relatively low vapor pressure and a normal boiling point of 152.2°C . Rationalize the differences of these physical properties from those of water.

44. Carbon diselenide (CSe_2) is a liquid at room temperature. The normal boiling point is 125°C , and the melting point is -45.5°C . Carbon disulfide (CS_2) is also a liquid at room temperature with normal boiling and melting points of 46.5°C and -111.6°C , respectively. How do the strengths of the intermolecular forces vary from CO_2 to CS_2 to CSe_2 ? Explain.

Structures and Properties of Solids

45. X rays from a copper X-ray tube ($\lambda = 1.54 \text{ \AA}$) were diffracted at an angle of 14.22 degrees by a crystal of silicon. Assuming first-order diffraction ($n = 1$ in the Bragg equation), what is the interplanar spacing in silicon?

46. X rays of wavelength $2.63 \text{ \AA}$ were used to analyze a crystal. The angle of first-order diffraction ($n = 1$ in the Bragg equation) was 15.55 degrees. What is the spacing between crystal planes, and what would be the angle for second-order diffraction ($n = 2$)?

47. Calcium has a cubic closest packed structure as a solid. Assuming that calcium has an atomic radius of 197 pm , calculate the density of solid calcium.

48. Nickel has a face-centered cubic unit cell. The density of nickel is 6.84 g/cm^3 . Calculate a value for the atomic radius of nickel.

49. Iridium (Ir) has a face-centered cubic unit cell with an edge length of 383.3 pm . Calculate the density of solid iridium.

50. You are given a small bar of an unknown metal X. You find the density of the metal to be 10.5 g/cm^3 . An X-ray diffraction experiment measures the edge of the face-centered cubic unit cell as $4.09 \text{ \AA}$ ($1 \text{ \AA} = 10^{-10} \text{ m}$). Identify X.

51. Titanium metal has a body-centered cubic unit cell. The density of titanium is 4.50 g/cm^3 . Calculate the edge length of the unit cell and a value for the atomic radius of titanium. (Hint: In a body-centered arrangement of spheres, the spheres touch across the body diagonal.)

52. Barium has a body-centered cubic structure. If the atomic radius of barium is 222 pm, calculate the density of solid barium.

53. What fraction of the total volume of a cubic closest packed structure is occupied by atoms? (Hint: $V_{\text{sphere}} = \frac{4}{3}\pi r^3$.) What fraction of the total volume of a simple cubic structure is occupied by atoms? Compare the answers.

54. Iron has a density of 7.86 g/cm³ and crystallizes in a body-centered cubic lattice. Show that only 68% of a body-centered lattice is actually occupied by atoms, and determine the atomic radius of iron.

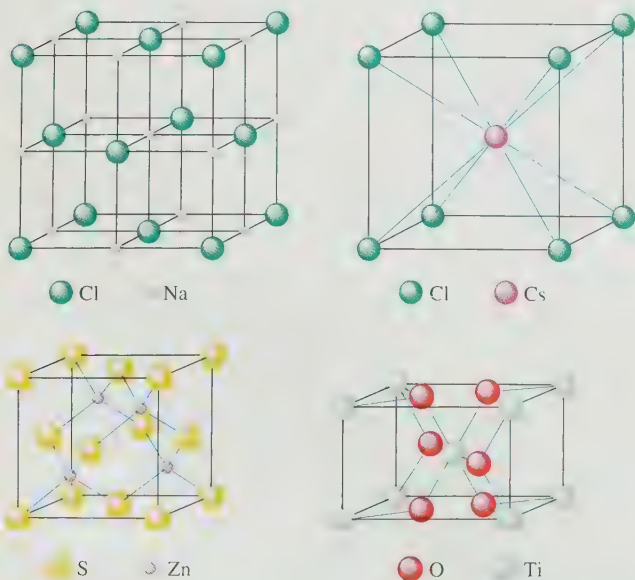
55. Selenium is a semiconductor used in photocopying machines. What type of semiconductor would be formed if a small amount of indium impurity is added to pure selenium?

56. The Group 3A/Group 5A semiconductors are composed of equal amounts of atoms from Group 3A and Group 5A, for example, InP and GaAs. These types of semiconductors are used in light-emitting diodes and solid-state lasers. What would you add to make a p-type semiconductor from pure GaAs? How would you dope pure GaAs to make an n-type semiconductor?

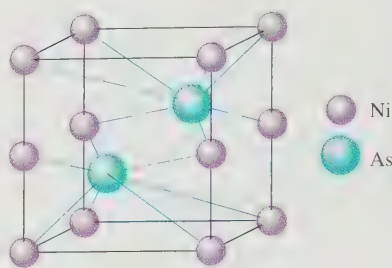
57. The band gap in aluminum phosphide (AlP) is 2.5 electronvolts (1 eV = 1.6×10^{-19} J). What wavelength of light is emitted by an AlP diode?

58. An aluminum antimonide solid-state laser emits light with a wavelength of 730. nm. Calculate the band gap in joules.

59. The structures of some common crystalline substances are shown below. Show that the net composition of each unit cell corresponds to the correct formula of each substance.



60. The unit cell for nickel arsenide is shown below. What is the formula of this compound?



61. Cobalt fluoride crystallizes in a closest packed array of fluoride ions with the cobalt ions filling one-half of the octahedral holes. What is the formula of this compound?

62. The compounds Na₂O, CdS, and ZrI₄ all can be described as cubic closest packed anions with the cations in tetrahedral holes. What fraction of the tetrahedral holes is occupied for each case?

63. A certain metal fluoride crystallizes in such a way that the fluoride ions occupy simple cubic lattice sites, while the metal ions occupy the body centers of *half* the cubes. What is the formula of the metal fluoride?

64. The structure of manganese fluoride can be described as a simple cubic array of manganese ions with fluoride ions at the center of each edge of the cubic unit cell. What is the charge of the manganese ions in this compound?

65. Magnesium oxide has the same structure as sodium chloride and has a density of 3.58 g/cm³. Calculate the edge length of the unit cell using this information. The ionic radii of Mg²⁺ and O²⁻ are 65 and 140. pm, respectively. Calculate the edge length of the unit cell from these data and compare it with your first answer.

66. The CsCl structure is a simple cubic array of chloride ions with a cesium ion at the center of each cubic array (see Exercise 59). Given that the density of cesium chloride is 3.97 g/cm³, and assuming that the chloride and cesium ions touch along the body diagonal of the cubic unit cell, calculate the distance between the centers of adjacent Cs⁺ and Cl⁻ ions in the solid. Compare this value with the expected distance based on the sizes of the ions. The ionic radius of Cs⁺ is 169 pm, and the ionic radius of Cl⁻ is 181 pm.

67. What type of solid will each of the following substances form?

- | | | |
|---------------------|---------------------|----------------------|
| a. CO ₂ | e. Ru | i. NaOH |
| b. SiO ₂ | f. I ₂ | j. U |
| c. Si | g. KBr | k. CaCO ₃ |
| d. CH ₄ | h. H ₂ O | l. PH ₃ |

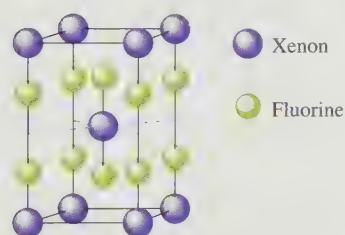
68. What type of solid will each of the following substances form?

- | | | |
|------------------|-----------------------------|--|
| a. diamond | e. KCl | i. Ar |
| b. PH_3 | f. quartz | j. Cu |
| c. H_2 | g. NH_4NO_3 | k. $\text{C}_6\text{H}_{12}\text{O}_6$ |
| d. Mg | h. SF_2 | |

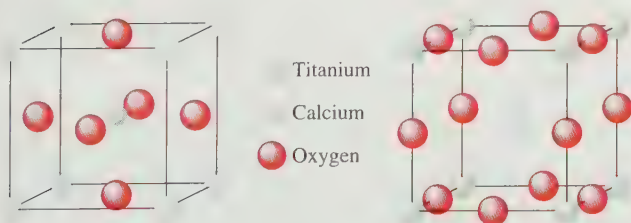
69. The memory metal, nitinol, is an alloy of nickel and titanium. It is called a *memory metal* because after being deformed, a piece of nitinol wire will return to its original shape. The structure of nitinol consists of a simple cubic array of Ni atoms and an inner penetrating simple cubic array of Ti atoms. In the extended lattice, a Ti atom is found at the center of a cube of Ni atoms; the reverse is also true.

- Describe the unit cell for nitinol.
- What is the empirical formula of nitinol?
- What are the coordination numbers (number of nearest neighbors) of Ni and Ti in nitinol?

70. The unit cell for a pure xenon fluoride compound is shown below. What is the formula of the compound?

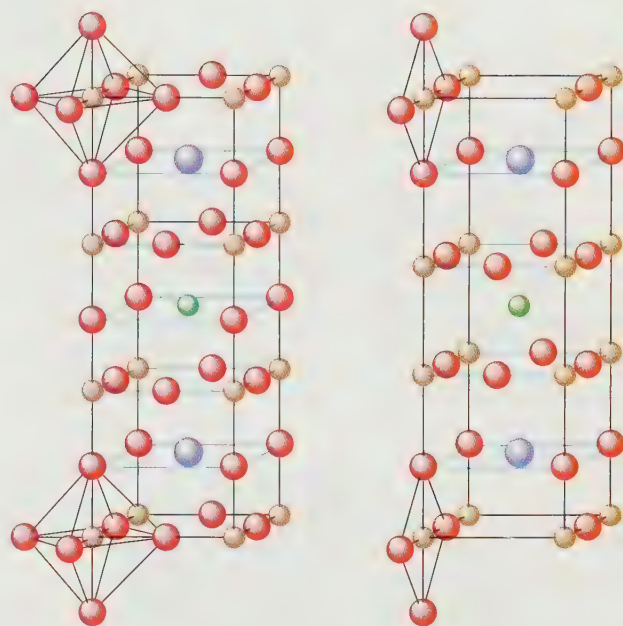


71. Perovskite is a mineral containing calcium, titanium, and oxygen. Two different representations of the unit cell are shown below. Show that both these representations give the same formula and the same number of oxygen atoms around each titanium atom.



72. A mineral crystallizes in a cubic closest packed array of sulfur ions with aluminum ions in one-half of the octahedral holes and zinc ions in one-eighth of the tetrahedral holes. What is the formula of this mineral?

73. Materials containing the elements Y, Ba, Cu, and O that are superconductors (electrical resistance equals zero) at tem-



(a) Ideal perovskite structure

(b) Actual structure of superconductor

peratures above that of liquid nitrogen were recently discovered. The structures of these materials are based on the perovskite structure. Were they to have the ideal perovskite structure, the superconductor would have the structure shown in part (a) of the figure above.

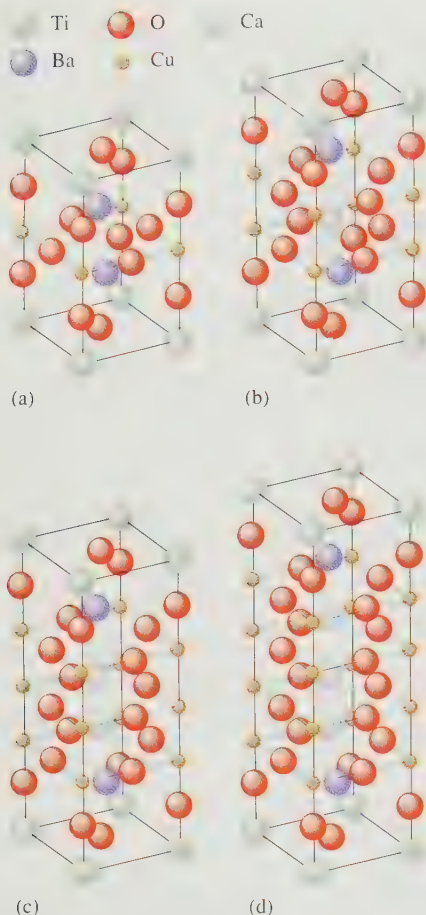
- What is the formula of this ideal perovskite material?
- How is this structure related to the perovskite structure shown in Exercise 71?

These materials, however, do not act as superconductors unless they are deficient in oxygen. The structure of the actual superconducting phase appears to be that shown in part (b) of the figure.

- What is the formula of this material?

74. The structures of another class of ceramic, high-temperature superconductors are shown in the figure on p. 504.

- Determine the formula of each of these four superconductors.
- One of the structural features that appears to be essential for high-temperature superconductivity is the presence of planar sheets of copper and oxygen atoms. As the number of sheets in each unit cell increases, the temperature for the onset of superconductivity increases. Order the four structures from lowest to the highest superconducting temperature.



- c. Assign oxidation states to Cu in each structure assuming Ti exists as Ti^{3+} . The oxidation states of Ca, Ba, and O are assumed to be +2, +2, and -2, respectively.
- d. It also appears that copper must display a mixture of oxidation states for a material to exhibit superconductivity. Explain how this occurs in these materials as well as in the superconductor in Exercise 73.

Phase Changes and Phase Diagrams

75. Plot the following data and determine ΔH_{vap} for magnesium and lithium. In which metal is the bonding stronger?

Vapor Pressure (mm Hg)	Temperature ($^{\circ}\text{C}$)	
	Li	Mg
1.	750.	620.
10.	890.	740.
100.	1080.	900.
400.	1240.	1040.
760.	1310.	1110.

76. From the following data for liquid nitric acid, determine its heat of vaporization and normal boiling point.

Temperature ($^{\circ}\text{C}$)	Vapor Pressure (mm Hg)
0	14.4
10.	26.6
20.	47.9
30.	81.3
40.	133
50.	208
80.	670.

77. In Breckenridge, Colorado, the typical atmospheric pressure is 520. torr. What is the boiling point of water ($\Delta H_{\text{vap}} = 40.7 \text{ kJ/mol}$) in Breckenridge?
78. What pressure would have to be applied to steam at $350.^{\circ}\text{C}$ to condense the steam to liquid water ($\Delta H_{\text{vap}} = 40.7 \text{ kJ/mol}$)?
79. The enthalpy of vaporization of mercury is 59.1 kJ/mol . The normal boiling point of mercury is 357°C . What is the vapor pressure of mercury at 25°C ?
80. The normal boiling point for acetone is 56.5°C . At an elevation of 5300 ft the atmospheric pressure is 630. torr. What would be the boiling point of acetone ($\Delta H_{\text{vap}} = 32.0 \text{ kJ/mol}$) at this elevation? What would be the vapor pressure of acetone at 25.0°C at this elevation?
81. A substance, X, has the following properties:

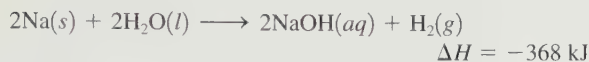
Specific Heat Capacities			
ΔH_{vap}	20. kJ/mol	C(s)	$3.0 \text{ J/g} \cdot ^{\circ}\text{C}$
ΔH_{fus}	5.0 kJ/mol	C(l)	$2.5 \text{ J/g} \cdot ^{\circ}\text{C}$
bp	75°C	C(g)	$1.0 \text{ J/g} \cdot ^{\circ}\text{C}$
mp	-15°C		

Sketch a heating curve for substance X starting at $-50.^{\circ}\text{C}$.

82. Given the data in Exercise 81 on substance X, calculate the energy that must be removed to convert substance X from a gas at $100.^{\circ}\text{C}$ to a solid at $-50.^{\circ}\text{C}$. Assume X has a polar mass of 75.0 g/mol .
83. How much energy does it take to convert 0.500 kg ice at $-20.^{\circ}\text{C}$ to steam at $250.^{\circ}\text{C}$? Specific heat capacities: ice, $2.1 \text{ J/g} \cdot ^{\circ}\text{C}$; liquid, $4.2 \text{ J/g} \cdot ^{\circ}\text{C}$; steam, $2.0 \text{ J/g} \cdot ^{\circ}\text{C}$, $\Delta H_{\text{vap}} = 40.7 \text{ kJ/mol}$, $\Delta H_{\text{fus}} = 6.02 \text{ kJ/mol}$.
84. Consider a 75.0-g sample of $\text{H}_2\text{O(g)}$ at 125°C . What phase or phases are present when 215 kJ of energy is removed from this sample? (See Exercise 83.)
85. An ice cube tray contains enough water at 22.0°C to make 18 ice cubes that each have a mass of 30.0 g . The tray is placed in a freezer that uses CF_2Cl_2 as a refrigerant. The heat of vaporization of CF_2Cl_2 is 158 J/g . What mass of CF_2Cl_2

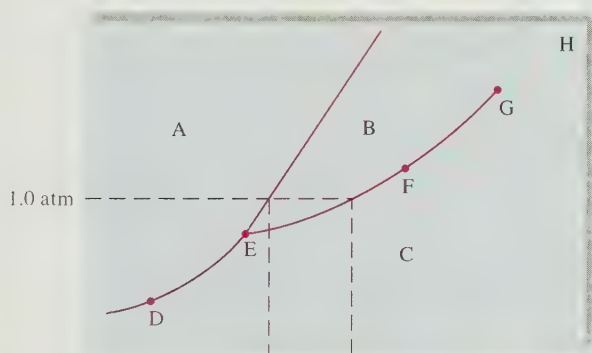
must be vaporized in the refrigeration cycle to convert all the water at 22.0°C to ice at -5.0°C ? The heat capacities for $\text{H}_2\text{O}(s)$ and $\text{H}_2\text{O}(l)$ are $2.08 \text{ J/g} \cdot ^{\circ}\text{C}$ and $4.18 \text{ J/g} \cdot ^{\circ}\text{C}$, respectively, and the enthalpy of fusion for ice is 6.02 kJ/mol .

86. A 0.250-g chunk of sodium metal is cautiously dropped into a mixture of 50.0 g of water and 50.0 g of ice, both at 0°C . The reaction is

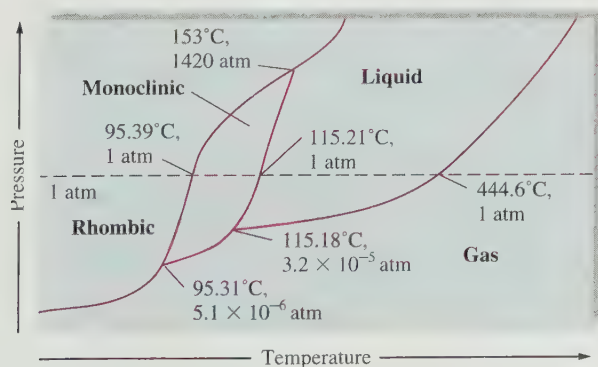


Will the ice melt? Assuming the final mixture has a specific heat capacity of $4.18 \text{ J/g} \cdot ^{\circ}\text{C}$, calculate the final temperature. The enthalpy of fusion for ice is 6.02 kJ/mol .

87. Consider the phase diagram given below. What phases are present at points A through H? Identify the triple point, normal boiling point, normal freezing point, and critical point. Which phase is denser, solid or liquid?



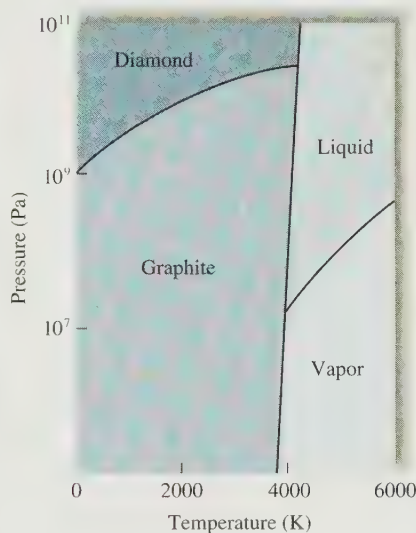
88. Sulfur exhibits two solid phases, rhombic and monoclinic. Use the accompanying phase diagram for sulfur to answer the following questions. (The phase diagram is not to scale.)
- How many triple points are in the phase diagram?
 - What phases are in equilibrium at each of the triple points?
 - What is the stable phase at 1 atm and 100°C ?
 - What are the normal melting point and the normal boiling point of sulfur?



- Which is the densest phase?
- At a pressure of $1.0 \times 10^{-5} \text{ atm}$, can rhombic sulfur sublime?
- What phase changes occur when the pressure on a sample of sulfur at 100°C is increased from $1.0 \times 10^{-8} \text{ atm}$ to 1500 atm?

89. Use the accompanying phase diagram for carbon to answer the following questions.

- How many triple points are in the phase diagram?
- What phases can coexist at each triple point?
- What happens if graphite is subjected to very high pressures at room temperature?
- If we assume that the density increases with an increase in pressure, which is more dense, graphite or diamond?



90. Like most substances, bromine exists in one of the three typical phases. Br_2 has a normal melting point of -7.2°C and a normal boiling point of 59°C . The triple point for Br_2 is -7.3°C and 40 torr, and the critical point is 320°C and 100 atm. Using this information, sketch a phase diagram for bromine indicating the points described above. Based on your phase diagram, order the three phases from least dense to most dense. What is the stable phase of Br_2 at room temperature and 1 atm? Under what temperature conditions can liquid bromine never exist? What phase changes occur as the temperature of a sample of bromine at 0.10 atm is increased from -50°C to 200°C ?

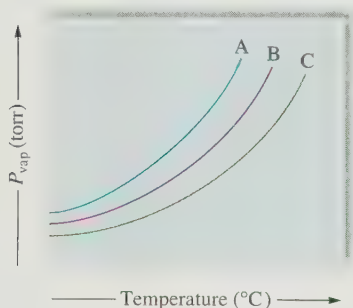
Additional Exercises

91. The nonpolar hydrocarbon $\text{C}_{25}\text{H}_{52}$ is a solid at room temperature. Its boiling point is greater than 400°C . Which has the stronger intermolecular forces, $\text{C}_{25}\text{H}_{52}$ or H_2O ? Explain your answer.

92. Rationalize the differences in physical properties in terms of intermolecular forces for the following organic compounds. Compare the first three substances with each other, compare the last three with each other, and then compare all six. Can you account for any anomalies?

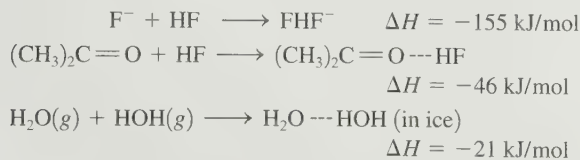
	bp (°C)	mp (°C)	ΔH_{vap} (kJ/mol)
Benzene, C_6H_6	80	6	33.9
Naphthalene, C_{10}H_8	218	80	51.5
Carbon tetra- chloride	76	-23	31.8
Acetone, CH_3COCH_3	56	-95	31.8
Acetic acid, $\text{CH}_3\text{CO}_2\text{H}$	118	17	39.7
Benzoic acid, $\text{C}_6\text{H}_5\text{CO}_2\text{H}$	249	122	68.2

93. Consider the following vapor pressure versus temperature plot for three different substances A, B, and C.



If the three substances are CH_4 , SiH_4 , and NH_3 , match each curve to the correct substance.

94. Consider the following enthalpy changes:



How do the strengths of hydrogen bonds vary with the electronegativity of the element to which hydrogen is bonded? Where in the preceding series would you expect hydrogen bonds of the following type to fall?



95. When a metal was exposed to X rays, it emitted X rays of a different wavelength. The emitted X rays were diffracted by a LiF crystal ($d = 201 \text{ pm}$), and first-order diffraction ($n = 1$ in

the Bragg equation) was detected at an angle of 34.68° . Calculate the wavelength of the X ray emitted by the metal.

96. The radius of gold is 144 pm , and the density is 19.32 g/cm^3 . Does elemental gold have a face-centered cubic structure or a body-centered cubic structure?
97. How could you tell experimentally if TiO_2 is an ionic solid or a network solid?
98. Boron nitride (BN) exists in two forms. The first is a slippery solid formed from the reaction of BCl_3 with NH_3 , followed by heating in an ammonia atmosphere at 750°C . Subjecting the first form of BN to a pressure of $85,000 \text{ atm}$ at 1800°C produces a second form that is the second hardest substance known. Both forms of BN remain solids to 3000°C . Suggest structures for the two forms of BN.
99. Consider the following data concerning four different substances.

Compound	Conducts Electricity as a Solid	Other Properties
B_2H_6	no	gas at 25°C
SiO_2	no	high mp
CsI	no	aqueous solution conducts electricity
W	yes	high mp

Label the four substances as either ionic, network, metallic, or molecular solids.

100. A 20.0-g sample of ice at -10.0°C is mixed with 100.0 g of water at 80.0°C . Calculate the final temperature of the mixture assuming no heat loss to the surroundings. The heat capacities of $\text{H}_2\text{O}(\text{s})$ and $\text{H}_2\text{O}(\text{l})$ are 2.08 and $4.18 \text{ J/g}\cdot^\circ\text{C}$, respectively, and the enthalpy of fusion for ice is 6.02 kJ/mol .
101. In regions with dry climates, evaporative coolers are used to cool air. A typical electric air conditioner is rated at $1.00 \times 10^4 \text{ Btu/h}$ (1 Btu , or British thermal unit = amount of energy to raise the temperature of 1 lb of water by 1°F). How much water must be evaporated each hour to dissipate as much heat as a typical electric air conditioner?
102. The critical point of NH_3 is 132°C and 111 atm , and the critical point of N_2 is -147°C and 34 atm . Which of these substances cannot be liquefied at room temperature no matter how much pressure is applied? Explain.

Challenge Problems

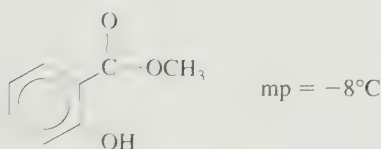
103. Using the heats of fusion and vaporization for water given in Exercise 83, calculate the change in enthalpy for the sublimation of water:



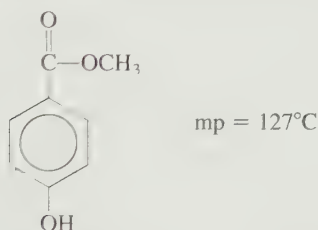
Using the ΔH value given in Exercise 94 and the number of hydrogen bonds formed with each water molecule, estimate

what portion of the intermolecular forces in ice can be accounted for by hydrogen bonding.

104. Oil of wintergreen, or methyl salicylate, has the following structure:



Methyl-4-hydroxybenzoate is another molecule with exactly the same molecular formula; it has the following structure:



Account for the large difference in the melting points of the two substances.

105. Consider the following melting point data:

Compound:	NaCl	MgCl ₂	AlCl ₃	SiCl ₄	PCl ₃	SCl ₂	Cl ₂
mp ($^{\circ}\text{C}$):	801	708	190	-70	-91	-78	-101
Compound:	NaF	MgF ₂	AlF ₃	SiF ₄	PF ₅	SF ₆	F ₂
mp ($^{\circ}\text{C}$):	997	1396	1040	-90	-94	-56	-220

Account for the trends in melting points in terms of interparticle forces.

106. MnO has either the NaCl type structure or the CsCl type structure (see Exercise 66). The edge length of the MnO unit cell is 4.47×10^{-8} cm and the density of MnO is 5.28 g/cm^3 .
- Does MnO crystallize in the NaCl or the CsCl type structure?
 - Assuming that the ionic radius of oxygen is 140. pm, estimate the ionic radius of manganese.
107. Some ionic compounds contain a mixture of different charged cations. For example, some titanium oxides contain a mixture of Ti^{2+} and Ti^{3+} ions. Consider a certain oxide of titanium that is 28.31% oxygen by mass and contains a mixture of Ti^{2+} and Ti^{3+} ions. Determine the formula of the compound and the relative numbers of Ti^{2+} and Ti^{3+} ions.
108. Spinel is a mineral that contains 37.9% aluminum, 17.1% magnesium, and 45.0% oxygen, by mass, and has a density of 3.57 g/cm^3 . The edge of the cubic unit cell measures 809 pm. How many of each type of atom are present in the unit cell?

109. Mn crystallizes in the same type of cubic unit cell as Cu. Assuming that the radius of Mn is 5.6% larger than the radius of Cu and the density of copper is 8.96 g/cm^3 , calculate the density of Mn.
110. You are asked to help set up a historical display in the park by stacking some cannonballs next to a Revolutionary War cannon. You are told to stack them by starting with a triangle in which each side is composed of four touching cannonballs. You are to continue stacking them until you have a single ball on the top centered over the middle of the triangular base.
- How many cannonballs do you need?
 - What type of closest packing is displayed by the cannonballs?
 - The four corners of the pyramid of cannonballs form the corners of what type of regular geometric solid?
111. Some water is placed in a sealed glass container connected to a vacuum pump (a device used to pump gases from a container), and the pump is turned on. The water appears to boil and then freezes. Explain these changes using the phase diagram for water. What would happen to the ice if the vacuum pump was left on indefinitely?
112. The molar enthalpy of vaporization of water at 373 K and 1.00 atm is 40.7 kJ/mol . What fraction of this energy is used to change the internal energy of the water, and what fraction is used to do work against the atmosphere? (*Hint*: Assume that water vapor is an ideal gas.)

Marathon Problem

This problem is designed to incorporate several concepts and techniques into one situation. Marathon Problems can be used in class by groups of students to help facilitate problem-solving skills.

113. General Zod has sold Lex Luther what Zod claims to be a new copper-colored form of kryptonite, the only substance that can harm Superman. Lex, not believing in honor among thieves, decided to carry out some tests on the supposed kryptonite. From previous tests, Lex knew that kryptonite is a metal having a specific heat capacity of $0.082 \text{ J/g} \cdot ^{\circ}\text{C}$ and a density of 9.2 g/mL .

Lex Luther's first experiment was an attempt to find the specific heat capacity of kryptonite. He dropped a $10 \pm 3 \text{ g}$ sample of the metal into a boiling water bath at a temperature of $100.0^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$. He waited until the metal had reached the bath temperature and then quickly transferred it to $100 \pm 3 \text{ g}$ of water that was contained in a calorimeter at an initial temperature of $25.0^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$. The final temperature of the metal and water was 25.2°C . Based on these results, is it possible to distinguish between copper and kryptonite? Explain.

When Lex found that his results from the first experiment were inconclusive, he decided to determine the density of the sample. He managed to steal a better balance and

determined the mass of another portion of the purported kryptonite to be $4 \text{ g} \pm 1 \text{ g}$. He dropped this sample into water contained in a 25-mL graduated cylinder and found that it displaced a volume of $0.42 \text{ mL} \pm 0.02 \text{ mL}$. Is the metal copper or kryptonite? Explain.

Lex was finally forced to determine the crystal structure of the metal General Zod had given him. He found that the cubic unit cell contained 4 atoms and had an edge length of 600. pm. Explain how this information enabled Lex to identify the metal as copper or kryptonite.

Will Lex be going after Superman with the kryptonite or seeking revenge on General Zod? What improvements could he have made in his experimental techniques to avoid performing the crystal structure determination?

Media Activities

- Open the Intermolecular Forces Understanding Concepts activity on the student CD to review types of intermolecular forces for covalent compounds. What type of intermolecular forces do nonpolar covalent compounds exhibit? How is size related to the strength of London dispersion forces? An extremely strong type of dipole-dipole force is hydrogen bonding. What three covalent bonds do you look for in order for a covalent compound to exhibit hydrogen bonding? How does the strength of ionic forces compare to hydrogen bonding?
 - Practice predicting the strongest type of intermolecular forces for various covalent compounds by doing the exercises in the activity. Predicting whether the compounds are polar or nonpolar is an important part of the exercise that requires you to predict molecular structures.
- Crystalline solids have a highly ordered structure. The smallest repeating unit in a crystalline solid is called the unit cell. Open the Unit Cells and Crystal Packing Visualization on the student CD to review three common types of cubic unit cells.
 - When discussing metals, we commonly assume that the metal atoms are uniform, hard spheres that occupy the lattice points of the unit cells. For each cubic unit cell, how many net spheres (atoms) are contained in a unit cell?
 - The atoms in a simple cubic unit cell are assumed to touch along the edges of the unit cell. With this in mind, how is the radius of an atom related to the edge length of the unit cell? Answer this same question for a body-centered unit cell and for a face-centered cubic unit cell. (*Hint:* The atoms are assumed to touch along the body diagonal in a body-centered cubic unit cell and to touch along the face diagonal in a face-centered cubic unit cell. You will also need to apply the Pythagorean theorem.)
 - A common application of the relationships discussed above is to estimate the density of various metals knowing the type of unit cell. Do Exercises 10.49 and 10.52 in the text to examine some typical problems of this nature. A closest packed structure has the atoms packed together in the most efficient way. What is the difference between hexagonal closest packing and cubic closest packing? Which cubic unit cell is present in cubic closest packing?
- Not all solids pack in a very ordered array. Amorphous solids show considerable disorder in their structure. Glass is a common example of an amorphous solid (see Figure 10.28 in the text). The primary component of glass is silica, which has an empirical formula of SiO_2 . From the formula of silica, one might expect SiO_2 and CO_2 to have similar structures; however, this is not the case. Compare and contrast the structure of CO_2 to that of silica.
 - Ceramics can also be based on silicon-oxygen bridged compounds (called silicates). However, other chemical forms of ceramics exist including materials made from oxygen and metals. An important property of some oxide ceramics is superconductivity. View the Magnetic Levitation by a Superconductor Visualization on the student CD to learn more about superconductivity. Unlike glass, these superconductivity ceramics are crystalline in nature. To learn more about the crystalline structures of these superconducting ceramics, do Exercises 10.73 and 10.74 in the text.
- Open the Changes of State Understanding Concepts activity on the student CD to review phase changes and heating curves.
 - When a solid converts to a liquid and then to a gas, what happens in terms of the intermolecular forces? Rationalize why ΔH_{vap} for water is over six times larger than ΔH_{fus} .
 - Go to the page with the heating curve. The heating curve has five basic parts to it. There are two plateau regions and three positive sloping lines in a typical heating curve. To calculate the energy necessary to convert some ice at a certain temperature below 0°C to gas at a temperature above 100°C , five quantities must be known: ΔH_{vap} , ΔH_{fus} , the specific heat capacity of gaseous water, the specific heat capacity of water, and the specific heat capacity of ice. Match these five quantities to the five parts in a typical heating curve. For H_2O , what temperature is the plateau at the lower temperature? the plateau at the higher energy? Do Exercise 10.83 in the text, which illustrates this type of calculation. Then do Exercise 10.81 in the text to test your ability to draw heating curves. Finally, try Exercises 10.85 and 10.100 for some variations on phase change energy calculations.
 - Heating curves only represent substances at one particular pressure (typically 1 atm). Phase diagrams represent stable phases of a substance at many temperatures and pressures. Sketch the phase diagram for water. What happens to the melting point of water as the external pressure increases? What happens to the boiling point as the external pressure increases? For more typical phase diagram questions, do Exercises 10.87, 10.88, and 10.89 in the text.
- Test your understanding of Chapter 10 material by taking the ACE quizzes on the student web site.



For additional web activities and other resources, visit the Zumdahl, *Chemistry*, Sixth Edition textbook site at <http://chemistry.college.hmco.com/students>.



Properties of Solutions

Most of the substances we encounter in daily life are mixtures: Wood, milk, gasoline, champagne, seawater, shampoo, steel, and air are common examples. When the components of a mixture are uniformly intermingled—that is, when a mixture is homogeneous—it is called a *solution*. Solutions can be gases, liquids, or solids, as shown in Table 11.1. However, we will be concerned in this chapter with the properties of liquid solutions, particularly those containing water. As we saw in Chapter 4, many essential chemical reactions occur in aqueous solutions because water is capable of dissolving so many substances.

TABLE 11.1 Various Types of Solutions

Example	State of Solution	State of Solute	State of Solvent
Air, natural gas	Gas	Gas	Gas
Vodka in water, antifreeze	Liquid	Liquid	Liquid
Brass	Solid	Solid	Solid
Carbonated water (soda)	Liquid	Gas	Liquid
Seawater, sugar solution	Liquid	Solid	Liquid
Hydrogen in platinum	Solid	Gas	Solid

Opals are formed from colloidal suspensions of silica when the liquid evaporates.

CONTENTS

- 11.1** Solution Composition
- 11.2** The Energies of Solution Formation
- 11.3** Factors Affecting Solubility
 - Structure Effects
 - Pressure Effects
 - Temperature Effects (for Aqueous Solutions)
- 11.4** The Vapor Pressures of Solutions
 - Nonideal Solutions
- 11.5** Boiling-Point Elevation and Freezing-Point Depression
 - Boiling-Point Elevation
 - Freezing-Point Depression
- 11.6** Osmotic Pressure
 - Reverse Osmosis
- 11.7** Colligative Properties of Electrolyte Solutions
- 11.8** Colloids

11.1 Solution Composition

A solute is the substance being dissolved.
The solvent is the dissolving medium.

$$\text{Molarity} = \frac{\text{moles of solute}}{\text{liters of solution}}$$

When liquids are mixed, the liquid present in the largest amount is called the *solvent*.

In very dilute aqueous solutions, the magnitude of the molality and the molarity are almost the same.

Because a mixture, unlike a chemical compound, has a variable composition, the relative amounts of substances in a solution must be specified. The qualitative terms *dilute* (relatively little solute present) and *concentrated* (relatively large amount of solute) are often used to describe solution content, but we need to define solution composition more precisely to perform calculations. For example, in dealing with the stoichiometry of solution reactions in Chapter 4, we found it useful to describe solution composition in terms of **molarity**, or the number of moles of solute per liter of solution (symbolized by M).

Other ways of describing solution composition are also useful. **Mass percent** (sometimes called *weight percent*) is the percent by mass of the solute in the solution:

$$\text{Mass percent} = \left(\frac{\text{mass of solute}}{\text{mass of solution}} \right) \times 100\%$$

Another way of describing solution composition is the **mole fraction** (symbolized by the Greek lowercase letter chi, χ), the ratio of the number of moles of a given component to the total number of moles of solution. For a two-component solution, where n_A and n_B represent the number of moles of the two components,

$$\text{Mole fraction of component A} = \chi_A = \frac{n_A}{n_A + n_B}$$

Still another way of describing solution composition is **molality** (symbolized by m), the number of moles of solute per *kilogram of solvent*:

$$\text{Molality} = \frac{\text{moles of solute}}{\text{kilogram of solvent}}$$

SAMPLE EXERCISE 11.1

Various Methods for Describing Solution Composition

A solution is prepared by mixing 1.00 g ethanol ($\text{C}_2\text{H}_5\text{OH}$) with 100.0 g water to give a final volume of 101 mL. Calculate the molarity, mass percent, mole fraction, and molality of ethanol in this solution.

SOLUTION

Since molarity depends on the volume of the solution, it changes slightly with temperature. Molality is independent of temperature because it depends only on mass.

Molarity: The moles of ethanol can be obtained from its molar mass (46.07 g/mol):

$$1.00 \text{ g C}_2\text{H}_5\text{OH} \times \frac{1 \text{ mol C}_2\text{H}_5\text{OH}}{46.07 \text{ g C}_2\text{H}_5\text{OH}} = 2.17 \times 10^{-2} \text{ mol C}_2\text{H}_5\text{OH}$$

$$\text{Volume} = 101 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 0.101 \text{ L}$$

$$\begin{aligned} \text{Molarity of C}_2\text{H}_5\text{OH} &= \frac{\text{moles of C}_2\text{H}_5\text{OH}}{\text{liters of solution}} = \frac{2.17 \times 10^{-2} \text{ mol}}{0.101 \text{ L}} \\ &= 0.215 \text{ M} \end{aligned}$$

Mass percent:

$$\begin{aligned} \text{Mass percent C}_2\text{H}_5\text{OH} &= \left(\frac{\text{mass of C}_2\text{H}_5\text{OH}}{\text{mass of solution}} \right) \times 100\% \\ &= \left(\frac{1.00 \text{ g C}_2\text{H}_5\text{OH}}{100.0 \text{ g H}_2\text{O} + 1.00 \text{ g C}_2\text{H}_5\text{OH}} \right) \times 100\% \\ &= 0.990\% \text{ C}_2\text{H}_5\text{OH} \end{aligned}$$

Mole fraction:

$$\begin{aligned}\text{Mole fraction of C}_2\text{H}_5\text{OH} &= \frac{n_{\text{C}_2\text{H}_5\text{OH}}}{n_{\text{C}_2\text{H}_5\text{OH}} + n_{\text{H}_2\text{O}}} \\ n_{\text{H}_2\text{O}} &= 100.0 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.0 \text{ g H}_2\text{O}} = 5.56 \text{ mol} \\ \chi_{\text{C}_2\text{H}_5\text{OH}} &= \frac{2.17 \times 10^{-2} \text{ mol}}{2.17 \times 10^{-2} \text{ mol} + 5.56 \text{ mol}} \\ &= \frac{2.17 \times 10^{-2}}{5.58} = 0.00389\end{aligned}$$

Molality:

$$\begin{aligned}\text{Molality of C}_2\text{H}_5\text{OH} &= \frac{\text{moles of C}_2\text{H}_5\text{OH}}{\text{kilogram of H}_2\text{O}} = \frac{2.17 \times 10^{-2} \text{ mol}}{100.0 \text{ g} \times \frac{1 \text{ kg}}{1000 \text{ g}}} \\ &= \frac{2.17 \times 10^{-2} \text{ mol}}{0.1000 \text{ kg}} \\ &= 0.217 \text{ m}\end{aligned}$$

See Exercises 11.25 through 11.27.

The definition of an equivalent depends on the reaction taking place in the solution.

The quantity we call *equivalent mass* here traditionally has been called *equivalent weight*.

Oxidation–reduction half-reactions were discussed in Section 4.10.

Another concentration measure sometimes encountered is **normality** (symbolized by *N*). Normality is defined as the number of *equivalents* per liter of solution, where the definition of an equivalent depends on the reaction taking place in the solution. *For an acid–base reaction*, the equivalent is the mass of acid or base that can furnish or accept exactly 1 mole of protons (H^+ ions). In Table 11.2 note, for example, that the equivalent mass of sulfuric acid is the molar mass divided by 2, since each mole of H_2SO_4 can furnish 2 moles of protons. The equivalent mass of calcium hydroxide is also half the molar mass, since each mole of $\text{Ca}(\text{OH})_2$ contains 2 moles of OH^- ions that can react with 2 moles of protons. The equivalent is defined so that 1 equivalent of acid will react with exactly 1 equivalent of base.

For oxidation–reduction reactions, the equivalent is defined as the quantity of oxidizing or reducing agent that can accept or furnish 1 mole of electrons. Thus 1 equivalent of reducing agent will react with exactly 1 equivalent of oxidizing agent. The equivalent mass of an oxidizing or reducing agent can be calculated from the

TABLE 11.2 The Molar Mass, Equivalent Mass, and Relationship of Molarity and Normality for Several Acids and Bases

Acid or Base	Molar Mass	Equivalent Mass	Relationship of Molarity and Normality
HCl	36.5	36.5	1 M = 1 N
H_2SO_4	98	$\frac{98}{2} = 49$	1 M = 2 N
NaOH	40	40	1 M = 1 N
$\text{Ca}(\text{OH})_2$	74	$\frac{74}{2} = 37$	1 M = 2 N

CHEMICAL IMPACT

Electronic Ink

The printed page has been a primary means of communication for over 3000 years, and researchers at the Massachusetts Institute of Technology (MIT) believe they have discovered why. It seems that the brain responds positively to fixed images on a sheet of paper, particularly those areas of the brain that store and process “spatial maps.” In comparison, information displayed on computer screens or TV screens seems to lack some of the visual signals that stimulate the learning centers of the brain to retain knowledge. While modern technology provides us with many other media by which we can communicate, the appeal of written words on a piece of paper remains. Surprisingly, the technology of printing has changed very little since the invention of the printing press—that is, until now.

In the past several years Joseph M. Jacobson and his students at MIT have developed a prototype of a self-printing page. The key to this self-printing “paper” is microencapsulation technology—the same technology that is used in “carbonless” carbon paper and “scratch-and-sniff” cologne and perfume advertisements in magazines. Jacobson’s system involves the use of millions of transparent fluid-filled capsules containing microscopic particles. These particles are colored and positively charged on one side and white and negatively charged on the other. When an electric field is selectively applied to the capsules, the white side of the microparticles can be oriented upward or the colored side can be caused to flip up. Appropriate application of an electric field can orient the particles in such a way as to produce words, and once the words have been created, virtually no more energy is needed to keep the particles in place. An image can be maintained on a page with consumption of only 50 millionths of an amp of power! The entire display is about 200 μm thick (2.5 times that of paper) and is so flexible and durable that it can be curled around a pencil and can operate at temperatures from -4 to 158°F . Presently, print resolution is not as good as a mod-

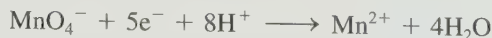


Signs like this one created by E Ink are the first to use electronic ink, which can be updated from a computer inside the store or from a remote location.

ern laser printer, but reduction of the microencapsulated particles from 50 to 40 μm should produce print that rivals the quality of the laser printer.

The first commercial applications of this technology are expected to appear in retail stores across the country in the form of electronic signs that can be updated instantly from a central location. The present technology is a long way from being able to create electronic books, but this is the eventual goal of Jacobson’s research team. It seems very likely that this electronic ink technology will contribute greatly to the evolution of the printed page over the next century.

number of electrons in its half-reaction. For example, MnO_4^- reacting in acidic solution absorbs five electrons to produce Mn^{2+} :



Since the MnO_4^- ion present in 1 mole of KMnO_4 consumes 5 moles of electrons, the equivalent mass is the molar mass divided by 5:

$$\text{Equivalent mass of KMnO}_4 = \frac{\text{molar mass}}{5} = \frac{158 \text{ g}}{5} = 31.6 \text{ g}$$

SAMPLE EXERCISE 11.2

Calculating Various Methods of Solution Composition from the Molarity

The electrolyte in automobile lead storage batteries is a 3.75 *M* sulfuric acid solution that has a density of 1.230 g/mL. Calculate the mass percent, molality, and normality of the sulfuric acid.

SOLUTION

The density of the solution in grams per liter is

$$1.230 \frac{\text{g}}{\text{mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 1.230 \times 10^3 \text{ g/L}$$

Thus 1 liter of this solution contains 1230. g of the mixture of sulfuric acid and water. Since the solution is 3.75 *M*, we know that 3.75 mol H₂SO₄ is present per liter of solution. The number of grams of H₂SO₄ present is

$$3.75 \text{ mol} \times \frac{98.1 \text{ g H}_2\text{SO}_4}{1 \text{ mol}} = 368 \text{ g H}_2\text{SO}_4$$

The amount of water present in 1 liter of solution is obtained from the difference

$$1230. \text{ g solution} - 368 \text{ g H}_2\text{SO}_4 = 862 \text{ g H}_2\text{O}$$

Since we now know the masses of the solute and solvent, we can calculate the mass percent.

$$\begin{aligned} \text{Mass percent H}_2\text{SO}_4 &= \frac{\text{mass of H}_2\text{SO}_4}{\text{mass of solution}} \times 100\% = \frac{368 \text{ g}}{1230. \text{ g}} \times 100\% \\ &= 29.9\% \text{ H}_2\text{SO}_4 \end{aligned}$$

From the moles of solute and the mass of solvent we can calculate the molality.

$$\begin{aligned} \text{Molality of H}_2\text{SO}_4 &= \frac{\text{moles H}_2\text{SO}_4}{\text{kilogram of H}_2\text{O}} \\ &= \frac{3.75 \text{ mol H}_2\text{SO}_4}{862 \text{ g H}_2\text{O} \times \frac{1 \text{ kg H}_2\text{O}}{1000 \text{ g H}_2\text{O}}} = 4.35 \text{ m} \end{aligned}$$

Since each sulfuric acid molecule can furnish two protons, 1 mol H₂SO₄ represents 2 equivalents. Thus a solution with 3.75 mol H₂SO₄ per liter contains $2 \times 3.75 = 7.50$ equivalents per liter, and the normality is 7.50 *N*.

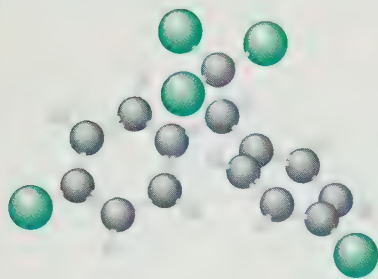
See Exercise 11.31.

11.2 The Energies of Solution Formation

Dissolving solutes in liquids is very common. We dissolve salt in the water used to cook vegetables, sugar in iced tea, stains in cleaning fluid, gaseous carbon dioxide in water to make soda water, ethanol in gasoline to make gasohol, and so on.



A modern 12-volt lead storage battery of the type used in automobiles.



DDT.

Polar solvents dissolve polar solutes; non-polar solvents dissolve nonpolar solutes.

The enthalpy of solution is the sum of the energies used in expanding both solvent and solute and the energy of solvent-solute interaction.

ΔH_1 is expected to be small for nonpolar solutes but can be large for large molecules.

Solubility is important in other ways. For example, because the pesticide DDT is fat-soluble, it is retained and concentrated in animal tissues, where it causes detrimental effects. This is why DDT, even though it is effective for killing mosquitos, has been banned in the United States. Also, the solubility of various vitamins is important in determining correct dosages. The insolubility of barium sulfate means it can be used safely to improve X rays of the gastrointestinal tract, even though Ba^{2+} ions are quite toxic.

What factors affect solubility? The cardinal rule of solubility is *like dissolves like*. We find that we must use a polar solvent to dissolve a polar or ionic solute and a nonpolar solvent to dissolve a nonpolar solute. Now we will try to understand why this behavior occurs. To simplify the discussion, we will assume that the formation of a liquid solution takes place in three distinct steps.

- ➡ **1** Separating the solute into its individual components (expanding the solute).
- ➡ **2** Overcoming intermolecular forces in the solvent to make room for the solute (expanding the solvent).
- ➡ **3** Allowing the solute and solvent to interact to form the solution.

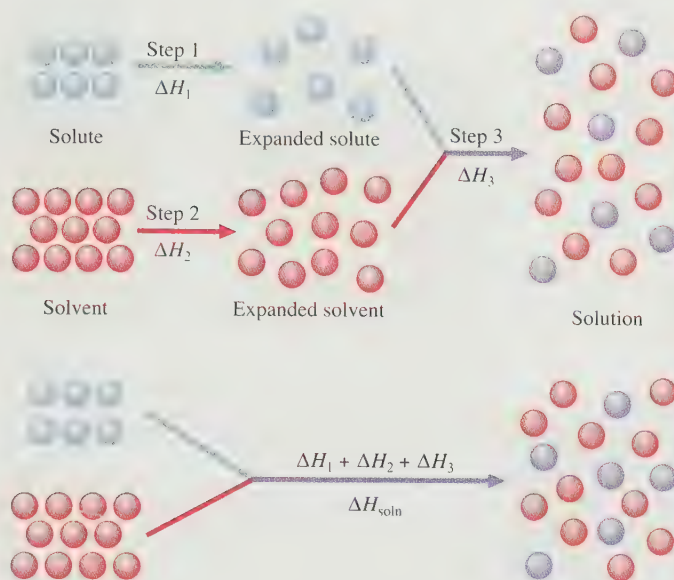
These steps are illustrated in Fig. 11.1. Steps 1 and 2 require energy, since forces must be overcome to expand the solute and solvent. Step 3 usually releases energy. In other words, steps 1 and 2 are endothermic, and step 3 is often exothermic. The enthalpy change associated with the formation of the solution, called the **enthalpy (heat) of solution** (ΔH_{soln}), is the sum of the ΔH values for the steps:

$$\Delta H_{\text{soln}} = \Delta H_1 + \Delta H_2 + \Delta H_3$$

where ΔH_{soln} may have a positive sign (energy absorbed) or a negative sign (energy released), as shown in Fig. 11.2.

To illustrate the importance of the various energy terms in the equation for ΔH_{soln} , we will consider two specific cases. First, we know that oil is not soluble in water. When oil tankers leak, the petroleum forms an oil slick that floats on the water and is eventually carried onto the beaches. We can explain the immiscibility of oil and water by considering the energy terms involved. Oil is a mixture of nonpolar molecules that interact through London dispersion forces, which depend on molecule size. We expect ΔH_1 to be small for a typical nonpolar solute, but it will be relatively large for the large oil molecules. The term ΔH_3 will be small, since interactions between the nonpolar solute molecules and the polar water molecules will be negligible. However, ΔH_2 will be large and positive because it takes considerable energy to overcome the hydrogen bonding forces among the water molecules to expand the solvent. Thus ΔH_{soln} will be large and positive because of the ΔH_1 and ΔH_2 terms. Since a large amount of energy would have to be expended to form an oil-water solution, this process does not occur to any appreciable extent. These same arguments hold true for any nonpolar solute and polar solvent—the combination of a nonpolar solute and a highly polar solvent is not expected to produce a solution.

As a second case, let's consider the solubility of an ionic solute, such as sodium chloride, in water. Here the term ΔH_1 is large and positive because the strong ionic forces in the crystal must be overcome, and ΔH_2 is large and positive because hydrogen bonds must be broken in the water. Finally, ΔH_3 is large and negative because of the strong interactions between the ions and the water molecules. In fact,

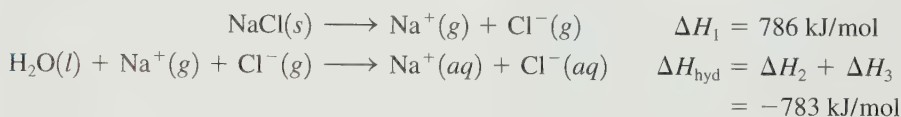
**FIGURE 11.1**

The formation of a liquid solution can be divided into three steps: (1) expanding the solute, (2) expanding the solvent, and (3) combining the expanded solute and solvent to form the solution.



Visualization: The Dissolution of a Solid in a Liquid

the exothermic and endothermic terms essentially cancel, as shown from the known values:

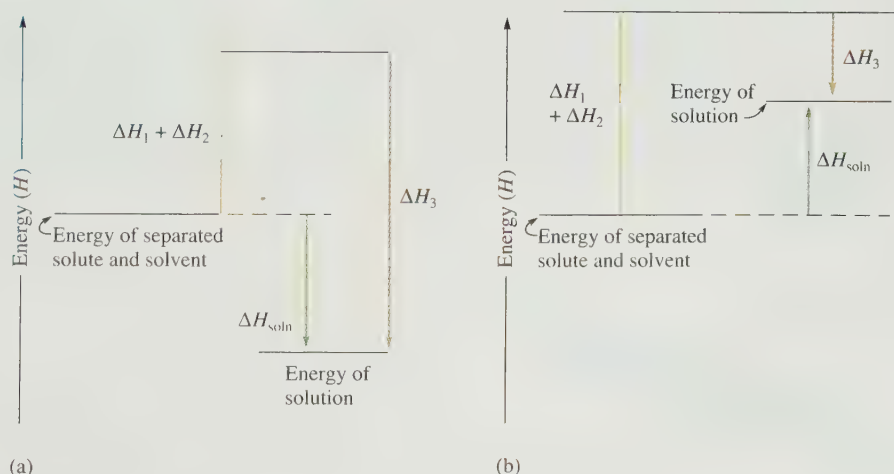


Here the **enthalpy (heat) of hydration** (ΔH_{hyd}) combines the terms ΔH_2 (for expanding the solvent) and ΔH_3 (for solvent–solute interactions). The heat of hydration represents the enthalpy change associated with the dispersal of a gaseous solute in water. Thus the heat of solution for dissolving sodium chloride is the sum of ΔH_1 and ΔH_{hyd} :

$$\Delta H_{\text{soln}} = 786 \text{ kJ/mol} - 783 \text{ kJ/mol} = 3 \text{ kJ/mol}$$

Note that ΔH_{soln} is small but positive; the dissolving process requires a small amount of energy. Then why is NaCl so soluble in water? The answer lies in nature's

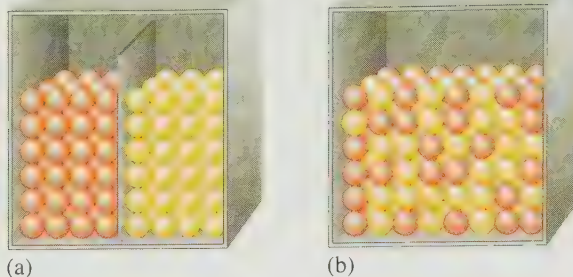
The factors that act as driving forces for a process are discussed more fully in Chapter 16.

**FIGURE 11.2**

The heat of solution (a) ΔH_{soln} has a negative sign (the process is exothermic) if step 3 releases more energy than that required by steps 1 and 2. (b) ΔH_{soln} has a positive sign (the process is endothermic) if steps 1 and 2 require more energy than is released in step 3. (If the energy changes for steps 1 and 2 equal that for step 3, then ΔH_{soln} is zero.)

FIGURE 11.3

(a) Orange and yellow spheres separated by a partition in a closed container. (b) The spheres after the partition is removed and the container has been shaken for some time.



Gasoline floating on water. Since gasoline is nonpolar, it is immiscible with water, because water contains polar molecules.

tendency toward higher probability of the mixed state. That is, processes naturally run in the direction that leads to the most probable state. For example, imagine equal numbers of orange and yellow spheres separated by a partition, as shown in Fig. 11.3(a). If we remove the partition and shake the container, the spheres will mix [Fig. 11.3(b)], and no amount of shaking will cause them to return to the state of separated orange and yellow. Why? The mixed state is simply much more likely to occur (more probable) than the original separate state because there are many more ways of placing the spheres to give a mixed state than a separated state. This is a general principle. *One factor that favors a process is an increase in probability.*

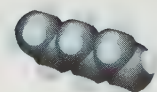
But energy considerations are also important. *Processes that require large amounts of energy tend not to occur.* Since dissolving 1 mole of solid NaCl requires only a small amount of energy, the solution forms, presumably because of the large increase in the probability of the state when the solute and solvent are mixed.

The various possible cases for solution formation are summarized in Table 11.3. Note that in two cases, polar–polar and nonpolar–nonpolar, the heat of solution is expected to be small. In these cases, the solution forms because of the increase in the probability of the mixed state. In the other cases (polar–nonpolar and nonpolar–polar), the heat of solution is expected to be large and positive, and the large quantity of energy required acts to prevent the solution from forming. Although this discussion has greatly oversimplified the complex driving forces for solubility, these ideas are a useful starting point for understanding the observation that *like dissolves like*.

SAMPLE EXERCISE 11.3

Differentiating Solvent Properties

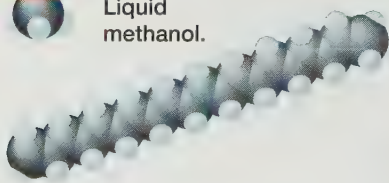
Decide whether liquid hexane (C_6H_{14}) or liquid methanol (CH_3OH) is the more appropriate solvent for the substances grease ($\text{C}_{20}\text{H}_{42}$) and potassium iodide (KI).



Hexane.



Liquid methanol.



Grease.

TABLE 11.3 The Energy Terms for Various Types of Solutes and Solvents

	ΔH_1	ΔH_2	ΔH_3	ΔH_{soln}	Outcome
Polar solute, polar solvent	Large	Large	Negative, large	Small	Solution forms
Nonpolar solute, polar solvent	Small	Large	Small	Positive, large	No solution forms
Nonpolar solute, nonpolar solvent	Small	Small	Small	Small	Solution forms
Polar solute, nonpolar solvent	Large	Small	Small	Positive, large	No solution forms

SOLUTION

Hexane is a nonpolar solvent because it contains C—H bonds. Thus hexane will work best for the nonpolar solute grease. Methanol has an O—H group that makes it significantly polar. Thus it will serve as the better solvent for the ionic solid KI.

See Exercises 11.37 through 11.39.

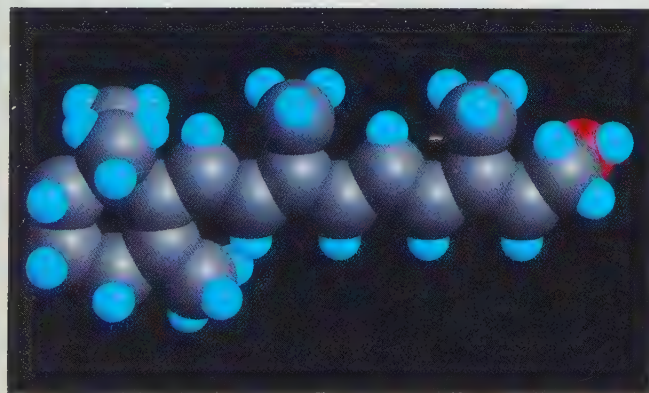
11.3 Factors Affecting Solubility

Structure Effects

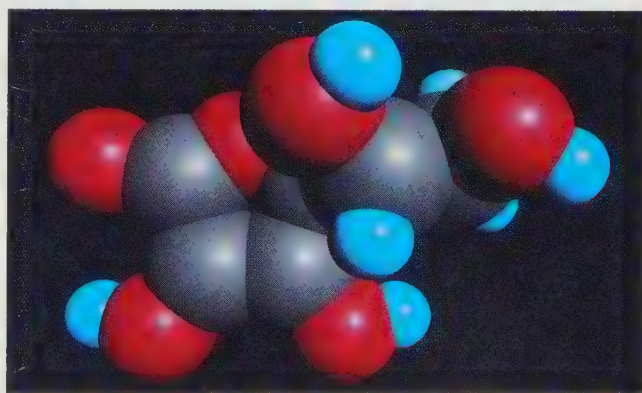
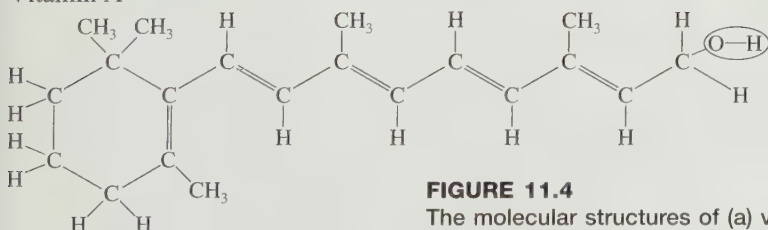
In the last section we saw that solubility is favored if the solute and solvent have similar polarities. Since it is the molecular structure that determines polarity, there should be a definite connection between structure and solubility. Vitamins provide an excellent example of the relationship among molecular structure, polarity, and solubility.

Recently, there has been considerable publicity about the pros and cons of consuming large quantities of vitamins. For example, large doses of vitamin C have been advocated to combat various illnesses, including the common cold. Vitamin E has been extolled as a youth-preserving elixir and a protector against the carcinogenic (cancer-causing) effects of certain chemicals. However, there are possible detrimental effects from taking large amounts of some vitamins, depending on their solubilities.

Vitamins can be divided into two classes: *fat-soluble* (vitamins A, D, E, and K) and *water-soluble* (vitamins B and C). The reason for the differing solubility characteristics can be seen by comparing the structures of vitamins A and C (Fig. 11.4).



Vitamin A



Vitamin C

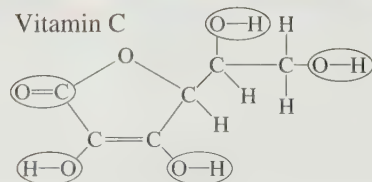


FIGURE 11.4

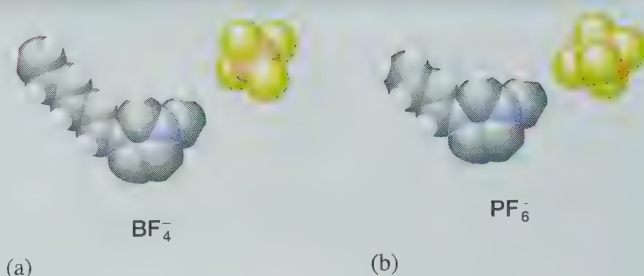
The molecular structures of (a) vitamin A (nonpolar, fat-soluble) and (b) vitamin C (polar, water-soluble). The circles in the structural formulas indicate polar bonds. Note that vitamin C contains far more polar bonds than vitamin A.

Ionic Liquids?

So far in this text, you have seen that ionic substances are stable solids with high melting points. For example, sodium chloride has a melting point near 800°C. One of the “hottest” areas of current chemical research is ionic liquids—substances composed of ions that are liquids at normal temperatures and pressures. This unusual behavior results from the differences in the sizes of the anions and cations in the ionic liquids. Dozens of small anions, such as BF_4^- (tetrafluoroborate) or PF_6^- (hexafluorophosphate), can be paired with thousands of large cations, such as 1-hexyl-3-methylimidazolium or 1-butyl-3-methylimidazolium (a and b respectively, in the accompanying figure). These substances remain liquids because the bulky, asymmetrical cations do not pack together efficiently with the smaller, symmetrical anions. In contrast, in sodium chloride the ions can pack very efficiently to form a compact, orderly arrangement, leading to maximum cation–anion attractions and thus a high melting point.

The excitement being generated by these ionic liquids arises from many factors. For one thing, almost an infinite variety of ionic liquids are possible due to the large variety of bulky cations and small anions available. According to Kenneth R. Seddon, Director of QUILL (Queen’s University Ionic Liquid Laboratory) in Northern Ireland, a *trillion* ionic liquids are possible. Another great advantage of these liquids is their long liquid range, typically from -100°C to 200°C .

In addition, the cations in the liquids can be designed to perform specific functions. For example, chemist James H. Davis, of the University of South Alabama in Mobile, has designed various cations that will attract potentially harmful



ions such as mercury, cadmium, uranium, and americium (the latter two are commonly found in nuclear waste materials) and leach them out of contaminated solutions. Davis has also developed cations that will remove H_2S (which produces SO_2 when the gas is burned) and CO_2 (which does not burn) from natural gas. Potentially, these ionic solutions might also be used to remove CO_2 from the exhaust gases of fossil-fuel–burning power plants to lessen the “greenhouse effect.”

The biggest obstacle to the widespread use of ionic liquids is their cost. Normal organic solvents used in industry typically cost a few cents per liter, but ionic liquids can cost hundreds of times that amount. However, the environmentally friendly nature of ionic liquids (they produce no vapors because the ions are not volatile) and the flexibility of these substances as reaction media make them very attractive. As a consequence, efforts are under way to make their use economically feasible.

The term *ionic liquid* may have seemed like an oxymoron in the past, but these substances have a very promising future.

Vitamin A, composed mostly of carbon and hydrogen atoms that have similar electronegativities, is virtually nonpolar. This causes it to be soluble in nonpolar materials such as body fat, which is also largely composed of carbon and hydrogen, but not soluble in polar solvents such as water. On the other hand, vitamin C has many polar O—H and C—O bonds, making the molecule polar and thus water-soluble. We often describe nonpolar materials such as vitamin A as *hydrophobic* (water-fearing) and polar substances such as vitamin C as *hydrophilic* (water-loving).

Because of their solubility characteristics, the fat-soluble vitamins can build up in the fatty tissues of the body. This has both positive and negative effects. Since these vitamins can be stored, the body can tolerate for a time a diet deficient in vitamins A, D, E, or K. Conversely, if excessive amounts of these vitamins are consumed, their buildup can lead to the illness *hypervitaminosis*.

In contrast, the water-soluble vitamins are excreted by the body and must be consumed regularly. This fact was first recognized when the British navy discov-



Carbonation in a bottle of soda.

William Henry (1774–1836), a close friend of John Dalton, formulated his law in 1801.

Henry's law holds only when there is no chemical reaction between the solute and solvent.

ered that scurvy, a disease often suffered by sailors, could be prevented if the sailors regularly ate fresh limes (which are a good source of vitamin C) when aboard ship (hence the name “limey” for the British sailor).

Pressure Effects

While pressure has little effect on the solubilities of solids or liquids, it does significantly increase the solubility of a gas. Carbonated beverages, for example, are always bottled at high pressures of carbon dioxide to ensure a high concentration of carbon dioxide in the liquid. The fizzing that occurs when you open a can of soda results from the escape of gaseous carbon dioxide because under these conditions the pressure of CO_2 above the solution is now much lower than that used in the bottling process.

The increase in gas solubility with pressure can be understood from Fig. 11.5. Figure 11.5(a) shows a gas in equilibrium with a solution; that is, the gas molecules are entering and leaving the solution at the same rate. If the pressure is suddenly increased [Fig. 11.5(b)], the number of gas molecules per unit volume increases, and the gas enters the solution at a higher rate than it leaves. As the concentration of dissolved gas increases, the rate of the escape of the gas also increases until a new equilibrium is reached [Fig. 11.5(c)], where the solution contains more dissolved gas than before.

The relationship between gas pressure and the concentration of dissolved gas is given by **Henry's law**:

$$C = kP$$

where C represents the concentration of the dissolved gas, k is a constant characteristic of a particular solution, and P represents the partial pressure of the gaseous solute above the solution. In words, Henry's law states that *the amount of a gas dissolved in a solution is directly proportional to the pressure of the gas above the solution*.

Henry's law is obeyed most accurately for dilute solutions of gases that do not dissociate in or react with the solvent. For example, Henry's law is obeyed by oxygen gas in water, but it does *not* correctly represent the behavior of gaseous hydrogen chloride in water because of the dissociation reaction

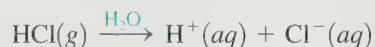
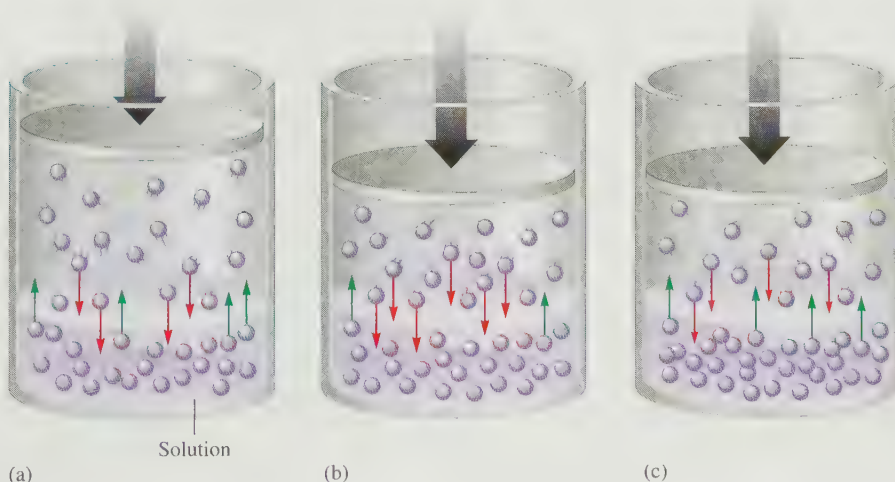


FIGURE 11.5

(a) A gaseous solute in equilibrium with a solution. (b) The piston is pushed in, which increases the pressure of the gas and the number of gas molecules per unit volume. This causes an increase in the rate at which the gas enters the solution, so the concentration of dissolved gas increases. (c) The greater gas concentration in the solution causes an increase in the rate of escape. A new equilibrium is reached.



SAMPLE EXERCISE 11.4

Calculations Using Henry's Law

A certain soft drink is bottled so that a bottle at 25°C contains CO₂ gas at a pressure of 5.0 atm over the liquid. Assuming that the partial pressure of CO₂ in the atmosphere is 4.0×10^{-4} atm, calculate the equilibrium concentrations of CO₂ in the soda both before and after the bottle is opened. The Henry's law constant for CO₂ in aqueous solution is 3.1×10^{-2} mol/L · atm at 25°C.

SOLUTION

We can write Henry's law for CO₂ as

$$C_{\text{CO}_2} = k_{\text{CO}_2} P_{\text{CO}_2}$$

where $k_{\text{CO}_2} = 3.1 \times 10^{-2}$ mol/L · atm. In the *unopened* bottle, $P_{\text{CO}_2} = 5.0$ atm and

$$C_{\text{CO}_2} = k_{\text{CO}_2} P_{\text{CO}_2} = (3.1 \times 10^{-2} \text{ mol/L} \cdot \text{atm})(5.0 \text{ atm}) = 0.16 \text{ mol/L}$$

In the *opened* bottle, the CO₂ in the soda eventually reaches equilibrium with the atmospheric CO₂, so $P_{\text{CO}_2} = 4.0 \times 10^{-4}$ atm and

$$C_{\text{CO}_2} = k_{\text{CO}_2} P_{\text{CO}_2} = \left(3.1 \times 10^{-2} \frac{\text{mol}}{\text{L} \cdot \text{atm}} \right) (4.0 \times 10^{-4} \text{ atm}) = 1.2 \times 10^{-5} \text{ mol/L}$$

Note the large change in concentration of CO₂. This is why soda goes “flat” after being open for a while.

See Exercises 11.43 and 11.44.

$\Delta H_{\text{soln}}^\circ$ refers to the formation of a 1.0 M ideal solution and is not necessarily relevant to the process of dissolving a solid in a saturated solution. Thus $\Delta H_{\text{soln}}^\circ$ is of limited use in predicting the variation of solubility with temperature.

Temperature Effects (for Aqueous Solutions)

Everyday experiences of dissolving substances such as sugar may lead you to think that solubility always increases with temperature. This is not the case. The dissolving of a solid occurs *more rapidly* at higher temperatures, but the amount of solid that can be dissolved may increase or decrease with increasing temperature. The effect of temperature on the solubility in water of several solids is shown in Fig. 11.6.

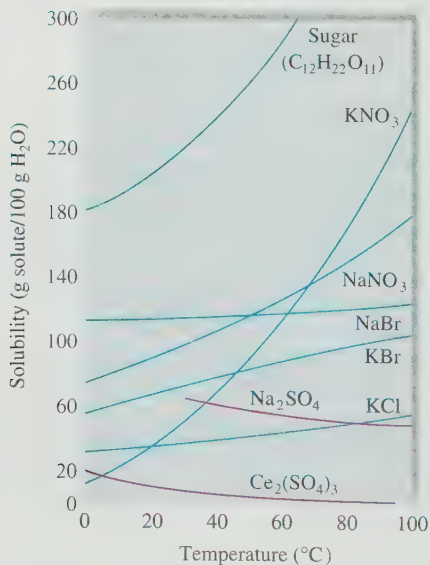


FIGURE 11.6

The solubilities of several solids as a function of temperature. Note that while most substances become more soluble in water with increasing temperature, sodium sulfate and cerium sulfate become less soluble.

CHEMICAL IMPACT

The Lake Nyos Tragedy

On August 21, 1986, a cloud of gas suddenly boiled from Lake Nyos in Cameroon, killing nearly 2000 people. Although at first it was speculated that the gas was hydrogen sulfide, it now seems clear it was carbon dioxide. What would cause Lake Nyos to emit this huge, suffocating cloud of CO_2 ? Although the answer may never be known for certain, many scientists believe that the lake suddenly “turned over,” bringing to the surface water that contained huge quantities of dissolved carbon dioxide. Lake Nyos is a deep lake that is thermally stratified: Layers of warm, less dense water near the surface float on the colder, denser water layers near the lake’s bottom. Under normal conditions the lake stays this way; there is little mixing among the different layers. Scientists believe that over hundreds or thousands of years, carbon dioxide gas had seeped into the cold water at the lake’s bottom and dissolved in great amounts because of the large pressure of CO_2 present (in accordance with Henry’s law). For some reason on August 21, 1986, the lake apparently suffered an overturn, possibly due to wind or to unusual cooling of the lake’s surface by monsoon clouds. This caused water that was greatly supersaturated with CO_2 to reach the surface and release tremendous quantities of gaseous CO_2 that suffocated thousands of humans and animals before they knew what hit them—a tragic, monumental illustration of Henry’s law.



Lake Nyos in Cameroon.

Since 1986 the scientists studying Lake Nyos and nearby Lake Monoun have observed a rapid recharging of the CO_2 levels in the deep waters of these lakes, causing concern that another deadly gas release could occur at any time. Apparently the only way to prevent such a disaster is to pump away the CO_2 -charged deep water in the two lakes. Scientists at a conference to study this problem in 1994 recommended such a solution, but it has not yet been funded by Cameroon.

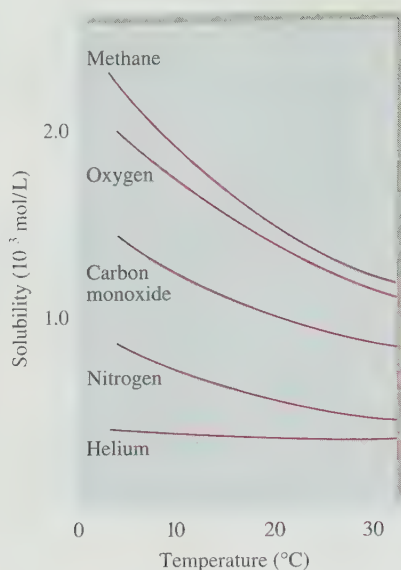
Note that although the solubility of most solids in water increases with temperature, the solubilities of some substances (such as sodium sulfate and cerium sulfate) decrease with increasing temperature.

Predicting the temperature dependence of solubility is very difficult. For example, although there is some correlation between the sign of $\Delta H_{\text{soln}}^\circ$ and the variation of solubility with temperature, important exceptions exist.* The only sure way to determine the temperature dependence of a solid’s solubility is by experiment.

The behavior of gases dissolving in water appears less complex. The solubility of a gas in water typically decreases with increasing temperature,† as is shown for several cases in Fig. 11.7. This temperature effect has important environmental implications because of the widespread use of water from lakes and rivers for industrial cooling. After being used, the water is returned to its natural source at a higher than ambient temperature (**thermal pollution** has occurred). Because it is warmer,

* For more information see R. S. Treptow, “Le Châtelier’s Principle Applied to the Temperature Dependence of Solubility,” *J. Chem. Ed.* **61** (1984): 499.

† The opposite behavior is observed for most nonaqueous solvents.

**FIGURE 11.7**

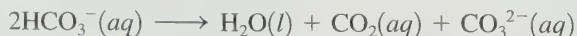
The solubilities of several gases in water as a function of temperature at a constant pressure of 1 atm of gas above the solution.

this water contains less than the normal concentration of oxygen and is also less dense; it tends to “float” on the colder water below, thus blocking normal oxygen absorption. This effect can be especially important in deep lakes. The warm upper layer can seriously decrease the amount of oxygen available to aquatic life in the deeper layers of the lake.

The decreasing solubility of gases with increasing temperature is also responsible for the formation of *boiler scale*. As we will see in more detail in Chapter 14, the bicarbonate ion is formed when carbon dioxide is dissolved in water containing the carbonate ion:



When the water also contains Ca^{2+} ions, this reaction is especially important—calcium bicarbonate is soluble in water, but calcium carbonate is insoluble. When the water is heated, the carbon dioxide is driven off. For the system to replace the lost carbon dioxide, the reverse reaction must occur:



This reaction, however, also increases the concentration of carbonate ions, causing solid calcium carbonate to form. This solid is the boiler scale that coats the walls of containers such as industrial boilers and tea kettles. Boiler scale reduces the efficiency of heat transfer and can lead to blockage of pipes (see Fig. 11.8).

**FIGURE 11.8**

A pipe with accumulated mineral deposits. The cross section clearly indicates the reduction in pipe capacity.

11.4 The Vapor Pressures of Solutions

Liquid solutions have physical properties significantly different from those of the pure solvent, a fact that has great practical importance. For example, we add antifreeze to the water in a car's cooling system to prevent freezing in winter and boiling in summer. We also melt ice on sidewalks and streets by spreading salt. These preventive measures work because of the solute's effect on the solvent's properties.

A nonvolatile solute has no tendency to escape from solution into the vapor phase.

The process described here is quite slow, taking several weeks to complete.

The presence of a nonvolatile solute reduces the tendency of solvent molecules to escape.

To explore how a nonvolatile solute affects a solvent, we will consider the experiment represented in Fig. 11.9, in which a sealed container encloses a beaker containing an aqueous sulfuric acid solution and a beaker containing pure water. Gradually, the volume of the sulfuric acid solution increases and the volume of the pure water decreases. Why? We can explain this observation if the vapor pressure of the pure solvent is greater than that of the solution. Under these conditions, the pressure of vapor necessary to achieve equilibrium with the pure solvent is greater than that required to reach equilibrium with the aqueous acid solution. Thus, as the pure solvent emits vapor to attempt to reach equilibrium, the aqueous sulfuric acid solution absorbs vapor to try to lower the vapor pressure toward its equilibrium value. This process results in a net transfer of water from the pure water through the vapor phase to the sulfuric acid solution. The system can reach an equilibrium vapor pressure only when all the water is transferred to the solution. This experiment is just one of many observations indicating that the presence of a *nonvolatile solute* lowers the vapor pressure of a solvent.

We can account for this behavior in terms of the simple model shown in Fig. 11.10. The dissolved nonvolatile solute decreases the number of solvent molecules

FIGURE 11.9

An aqueous solution and pure water in a closed environment. (a) Initial stage. (b) After a period of time, the water is transferred to the solution.

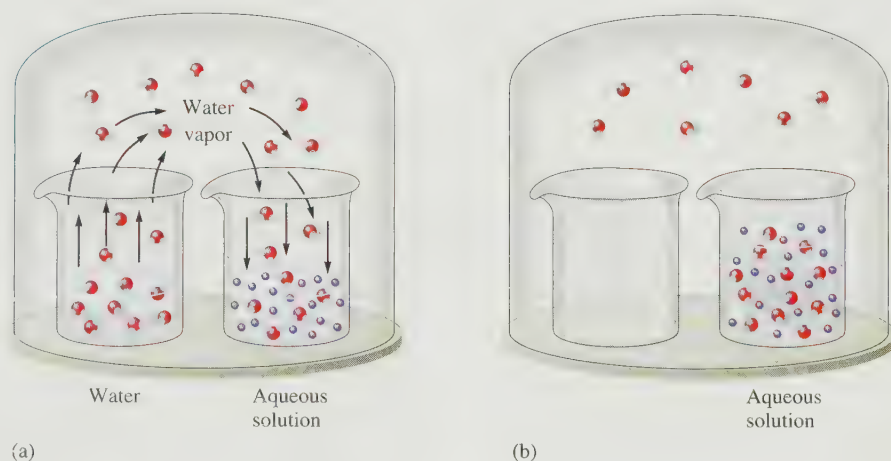
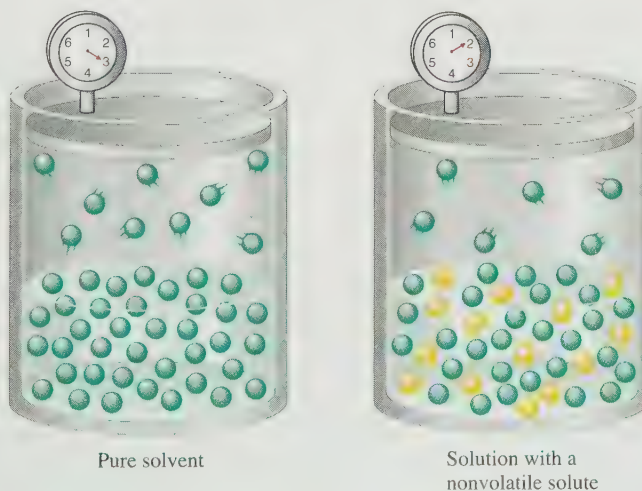
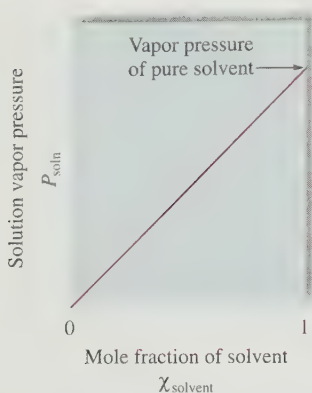


FIGURE 11.10

The presence of a nonvolatile solute inhibits the escape of solvent molecules from the liquid and so lowers the vapor pressure of the solvent.



**FIGURE 11.11**

For a solution that obeys Raoult's law, a plot of P_{soln} versus χ_{solvent} gives a straight line.

Raoult's law states that the vapor pressure of a solution is directly proportional to the mole fraction of solvent present.

per unit volume and it should proportionately lower the escaping tendency of the solvent molecules. For example, in a solution consisting of half nonvolatile solute molecules and half solvent molecules, we might expect the observed vapor pressure to be half that of the pure solvent, since only half as many molecules can escape. In fact, this is what is observed.

Detailed studies of the vapor pressures of solutions containing nonvolatile solutes were carried out by François M. Raoult (1830–1901). His results are described by the equation known as **Raoult's law**:

$$P_{\text{soln}} = \chi_{\text{solvent}} P_{\text{solvent}}^0$$

where P_{soln} is the observed vapor pressure of the solution, χ_{solvent} is the mole fraction of solvent, and P_{solvent}^0 is the vapor pressure of the pure solvent. Note that for a solution of half solute and half solvent molecules, χ_{solvent} is 0.5, so the vapor pressure of the solution is half that of the pure solvent. On the other hand, for a solution in which three-fourths of the solution molecules are solvent, $\chi_{\text{solvent}} = \frac{3}{4} = 0.75$, and $P_{\text{soln}} = 0.75P_{\text{solvent}}^0$. The idea is that the nonvolatile solute simply dilutes the solvent.

Raoult's law is a linear equation of the form $y = mx + b$, where $y = P_{\text{soln}}$, $x = \chi_{\text{solvent}}$, $m = P_{\text{solvent}}^0$, and $b = 0$. Thus a plot of P_{soln} versus χ_{solvent} gives a straight line with a slope equal to P_{solvent}^0 , as shown in Fig. 11.11.

SAMPLE EXERCISE 11.5

Calculating the Vapor Pressure of a Solution

Calculate the expected vapor pressure at 25°C for a solution prepared by dissolving 158.0 g of common table sugar (sucrose, molar mass = 342.3 g/mol) in 643.5 cm³ of water. At 25°C, the density of water is 0.9971 g/cm³ and the vapor pressure is 23.76 torr.

SOLUTION

We will use Raoult's law in the form

$$P_{\text{soln}} = \chi_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}}^0$$

To calculate the mole fraction of water in the solution, we must first determine the number of moles of sucrose:

$$\begin{aligned} \text{Moles of sucrose} &= 158.0 \text{ g sucrose} \times \frac{1 \text{ mol sucrose}}{342.3 \text{ g sucrose}} \\ &= 0.4616 \text{ mol sucrose} \end{aligned}$$

To determine the moles of water present, we first convert volume to mass using the density:

$$643.5 \text{ cm}^3 \text{ H}_2\text{O} \times \frac{0.9971 \text{ g H}_2\text{O}}{\text{cm}^3 \text{ H}_2\text{O}} = 641.6 \text{ g H}_2\text{O}$$

The number of moles of water is therefore

$$641.6 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.01 \text{ g H}_2\text{O}} = 35.63 \text{ mol H}_2\text{O}$$

CHEMICAL IMPACT

Spray Power

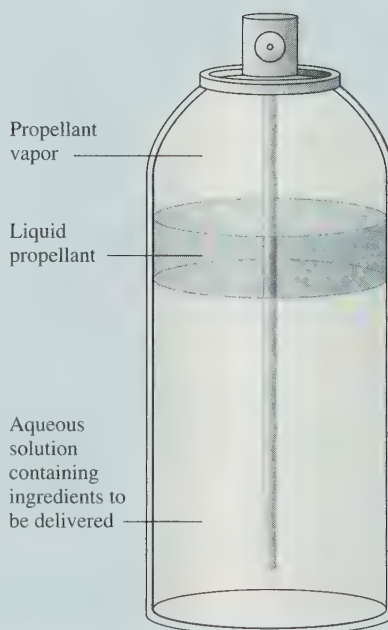
Products in aerosol cans are widely used in our society. We use hairsprays, mouth sprays, shaving cream, whipped cream, spray paint, spray cleaners, and many others. As in the case of most consumer products, chemistry plays an important role in making aerosol products work.

An aerosol is a mixture of small particles (solids or liquids) dispersed in some sort of medium (a gas or a liquid). An inspection of the ingredients in an aerosol can reveals a long list of chemical substances, all of which fall into one of three categories: (1) an active ingredient, (2) an inactive ingredient, or (3) a propellant. The active ingredients perform the functions for which the product was purchased (for example, the resins in hairspray). It is very important that the contents of an aerosol can be chemically compatible. If an undesired chemical reaction were to occur inside the can, it is likely that the product would be unable to perform its function. The inactive ingredients serve to keep the product properly mixed and prevent chemical reactions within the can prior to application. The propellant delivers the product out of the can.

Most aerosol products contain liquefied hydrocarbon propellants* such as propane (C_3H_8) and butane (C_4H_{10}). While these molecules are extremely flammable, they are excellent propellants, and they also help to disperse and mix the components of the aerosol can as they are delivered. These propellants have critical temperatures above room temperature, which means that the intermolecular forces among their molecules are strong enough to form a liquid when pressure is applied. In the highly pressurized aerosol can, the liquid phase of the propellant is in equilibrium with the gaseous phase of the propellant in the head space of the can. The ability of the propellant to maintain this equilibrium is the key to how the aerosol can works. All aerosol cans are constructed in a similar way (see accompanying diagram). At the top of the can is a valve (acts to open and seal the can) and an actuator (to open the valve). Pushing the actuator opens the valve, and the propellant gas escapes through a long tube (the dip tube) that extends from the bottom of the can. With the valve open, the propellant, at a greater pressure than the atmosphere, escapes through the dip tube, carrying the active ingredient(s) with it. The rapidly expanding gas propels the contents from the can and in some instances (for example, shaving cream, carpet shampoo) produces a foam. After each use, the remaining pro-



Insecticide is sprayed from an aerosol can.



An aerosol can for delivery of an active ingredient dissolved in an aqueous solution.

pellant in the can reestablishes equilibrium between the liquid and gaseous phases, keeping the pressure constant within the can as long as sufficient propellant remains. The trick is to have the active and inactive ingredients and the propellant run out at the same time. Given the nature of the most common propellants, you can understand the warning about not putting the “empty” cans in a fire.

*For foods delivered by aerosol cans, propane and butane are obviously not appropriate propellants. For substances such as whipped cream, the propellant N_2O is often used.

The mole fraction of water in the solution is

$$\begin{aligned}\chi_{\text{H}_2\text{O}} &= \frac{\text{mol H}_2\text{O}}{\text{mol H}_2\text{O} + \text{mol sucrose}} = \frac{35.63 \text{ mol}}{35.63 \text{ mol} + 0.4616 \text{ mol}} \\ &= \frac{35.63 \text{ mol}}{36.09 \text{ mol}} = 0.9873\end{aligned}$$

Then $P_{\text{soln}} = \chi_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}}^0 = (0.9873)(23.76 \text{ torr}) = 23.46 \text{ torr}$

Thus the vapor pressure of water has been lowered from 23.76 torr in the pure state to 23.46 torr in the solution. The vapor pressure has been lowered by 0.30 torr.

See Exercises 11.45 and 11.46.

The phenomenon of the lowering of the vapor pressure gives us a convenient way to “count” molecules and thus provides a means for experimentally determining molar masses. Suppose a certain mass of a compound is dissolved in a solvent and the vapor pressure of the resulting solution is measured. Using Raoult’s law, we can determine the number of moles of solute present. Since the mass of this number of moles is known, we can calculate the molar mass.

We also can use vapor pressure measurements to characterize solutions. For example, 1 mole of sodium chloride dissolved in water lowers the vapor pressure approximately twice as much as expected because the solid has two ions per formula unit, which separate when it dissolves. Thus vapor pressure measurements can give valuable information about the nature of the solute after it dissolves.

The lowering of vapor pressure depends on the number of solute particles present in the solution.

Calculating the Vapor Pressure of a Solution Containing Ionic Solute

SAMPLE EXERCISE 11.6

Predict the vapor pressure of a solution prepared by mixing 35.0 g solid Na_2SO_4 (molar mass = 142 g/mol) with 175 g water at 25°C. The vapor pressure of pure water at 25°C is 23.76 torr.

SOLUTION

First, we need to know the mole fraction of H_2O .

$$\begin{aligned}n_{\text{H}_2\text{O}} &= 175 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.0 \text{ g H}_2\text{O}} = 9.72 \text{ mol H}_2\text{O} \\ n_{\text{Na}_2\text{SO}_4} &= 35.0 \text{ g Na}_2\text{SO}_4 \times \frac{1 \text{ mol Na}_2\text{SO}_4}{142 \text{ g Na}_2\text{SO}_4} = 0.246 \text{ mol Na}_2\text{SO}_4\end{aligned}$$

It is essential to recognize that when 1 mole of solid Na_2SO_4 dissolves, it produces 2 mol Na^+ ions and 1 mol SO_4^{2-} ions. Thus the number of solute particles present in this solution is three times the number of moles of solute dissolved:

$$\begin{aligned}n_{\text{solute}} &= 3(0.246) = 0.738 \text{ mol} \\ \chi_{\text{H}_2\text{O}} &= \frac{n_{\text{H}_2\text{O}}}{n_{\text{solute}} + n_{\text{H}_2\text{O}}} = \frac{9.72 \text{ mol}}{0.738 \text{ mol} + 9.72 \text{ mol}} = \frac{9.72}{10.458} = 0.929\end{aligned}$$

Now we can use Raoult’s law to predict the vapor pressure:

$$P_{\text{soln}} = \chi_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}}^0 = (0.929)(23.76 \text{ torr}) = 22.1 \text{ torr}$$

See Exercise 11.48.

**FIGURE 11.12**

When a solution contains two volatile components, both contribute to the total vapor pressure. Note that in this case the solution contains equal numbers of the components  and  but the vapor contains more  than . This means that component  is more volatile (has a higher vapor pressure as a pure liquid) than component .

Strong solute–solvent interaction gives a vapor pressure lower than that predicted by Raoult’s law.

Nonideal Solutions

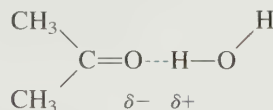
So far we have assumed that the solute is nonvolatile and so does not contribute to the vapor pressure over the solution. However, for liquid–liquid solutions where both components are volatile, a modified form of Raoult’s law applies:

$$P_{\text{TOTAL}} = P_A + P_B = \chi_A P_A^0 + \chi_B P_B^0$$

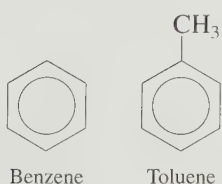
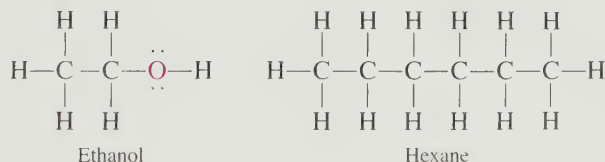
where P_{TOTAL} represents the total vapor pressure of a solution containing A and B, χ_A and χ_B are the mole fractions of A and B, P_A^0 and P_B^0 are the vapor pressures of pure A and pure B, and P_A and P_B are the partial pressures resulting from molecules of A and of B in the vapor above the solution (see Fig. 11.12).

A liquid–liquid solution that obeys Raoult’s law is called an **ideal solution**. Raoult’s law is to solutions what the ideal gas law is to gases. As with gases, ideal behavior for solutions is never perfectly achieved but is sometimes closely approached. Nearly ideal behavior is often observed when the solute–solute, solvent–solvent, and solute–solvent interactions are very similar. That is, in solutions where the solute and solvent are very much alike, the solute simply acts to dilute the solvent. However, if the solvent has a special affinity for the solute, such as if hydrogen bonding occurs, the tendency of the solvent molecules to escape will be lowered more than expected. The observed vapor pressure will be *lower* than the value predicted by Raoult’s law; there will be a *negative deviation from Raoult’s law*.

When a solute and solvent release large quantities of energy in the formation of a solution, that is, when ΔH_{soln} is large and negative, we can assume that strong interactions exist between the solute and solvent. In this case we expect a negative deviation from Raoult’s law, because both components will have a lower escaping tendency in the solution than in the pure liquids. This behavior is illustrated by an acetone–water solution, where the molecules can hydrogen bond effectively:



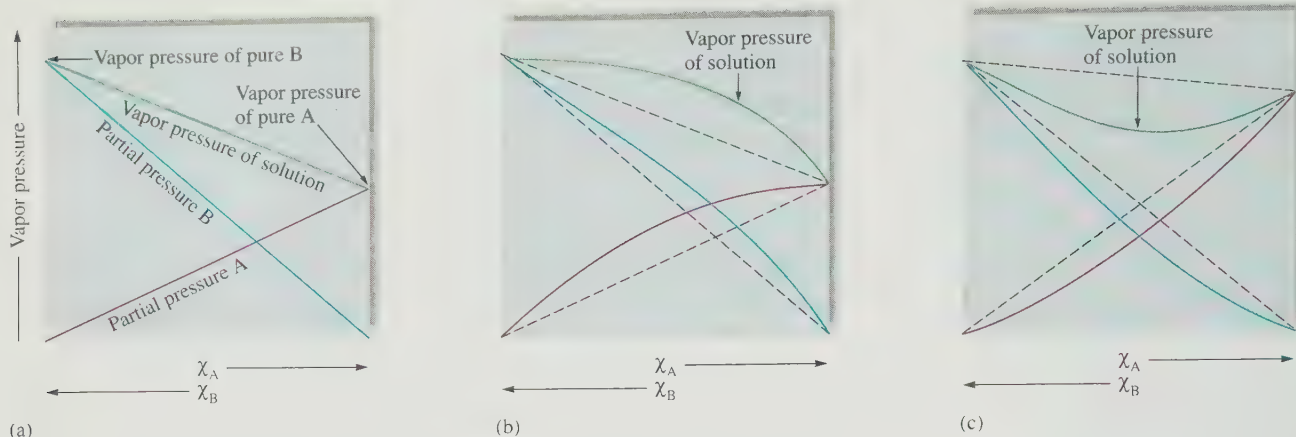
In contrast, if two liquids mix endothermically, it indicates that the solute–solvent interactions are weaker than the interactions among the molecules in the pure liquids. More energy is required to expand the liquids than is released when the liquids are mixed. In this case the molecules in the solution have a higher tendency to escape than expected, and *positive* deviations from Raoult’s law are observed (see Fig. 11.13). An example of this case is provided by a solution of ethanol and hexane, whose Lewis structures are as follows:



The polar ethanol and the nonpolar hexane molecules are not able to interact effectively. Thus the enthalpy of solution is positive, as is the deviation from Raoult’s law.

Finally, for a solution of very similar liquids, such as benzene and toluene (shown in margin), the enthalpy of solution is very close to zero, and thus the solution closely obeys Raoult’s law (ideal behavior).

A summary of the behavior of various types of solutions is given in Table 11.4.

**FIGURE 11.13**

Vapor pressure for a solution of two volatile liquids. (a) The behavior predicted for an ideal liquid-liquid solution by Raoult's law. (b) A solution for which P_{TOTAL} is larger than the value calculated from Raoult's law. This solution shows a positive deviation from Raoult's law. (c) A solution for which P_{TOTAL} is smaller than the value calculated from Raoult's law. This solution shows a negative deviation from Raoult's law.

SAMPLE EXERCISE 11.7**Calculating the Vapor Pressure of a Solution Containing Two Liquids**

A solution is prepared by mixing 5.81 g acetone ($\text{C}_3\text{H}_6\text{O}$, molar mass = 58.1 g/mol) and 11.9 g chloroform (HCCl_3 , molar mass = 119.4 g/mol). At 35°C, this solution has a total vapor pressure of 260. torr. Is this an ideal solution? The vapor pressures of pure acetone and pure chloroform at 35°C are 345 and 293 torr, respectively.

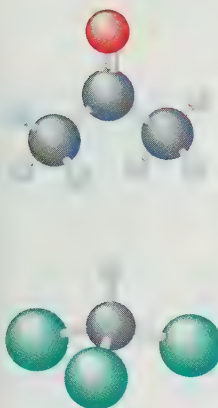
SOLUTION

To decide whether this solution behaves ideally, we first calculate the expected vapor pressure using Raoult's law:

$$P_{\text{TOTAL}} = \chi_A P_A^0 + \chi_C P_C^0$$

TABLE 11.4 Summary of the Behavior of Various Types of Solutions

Interactive Forces Between Solute (A) and Solvent (B) Particles	ΔH_{soln}	ΔT for Solution Formation	Deviation from Raoult's Law	Example
$A \leftrightarrow A, B \leftrightarrow B \equiv A \leftrightarrow B$	Zero	Zero	None (ideal solution)	Benzene-toluene
$A \leftrightarrow A, B \leftrightarrow B < A \leftrightarrow B$	Negative (exothermic)	Positive	Negative	Acetone-water
$A \leftrightarrow A, B \leftrightarrow B > A \leftrightarrow B$	Positive (endothermic)	Negative	Positive	Ethanol-hexane



Acetone and chloroform.

In this case, the usually nonpolar C—H bond is strongly polarized by the three attached, highly electronegative chlorine, thus producing hydrogen bonding.

where A stands for acetone and C stands for chloroform. The calculated value can then be compared with the observed vapor pressure.

First, we must calculate the number of moles of acetone and chloroform:

$$5.81 \text{ g acetone} \times \frac{1 \text{ mol acetone}}{58.1 \text{ g acetone}} = 0.100 \text{ mol acetone}$$

$$11.9 \text{ g chloroform} \times \frac{1 \text{ mol chloroform}}{119 \text{ g chloroform}} = 0.100 \text{ mol chloroform}$$

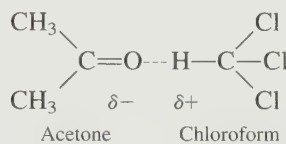
Since the solution contains equal numbers of moles of acetone and chloroform, that is,

$$\chi_A = 0.500 \quad \text{and} \quad \chi_C = 0.500$$

the expected vapor pressure is

$$P_{\text{TOTAL}} = (0.500)(345 \text{ torr}) + (0.500)(293 \text{ torr}) = 319 \text{ torr}$$

Comparing this value with the observed pressure of 260. torr shows that the solution does not behave ideally. The observed value is lower than that expected. This negative deviation from Raoult's law can be explained in terms of the following dipole-dipole interaction:



which lowers the tendency of these molecules to escape from the solution.

See Exercises 11.55 and 11.56.

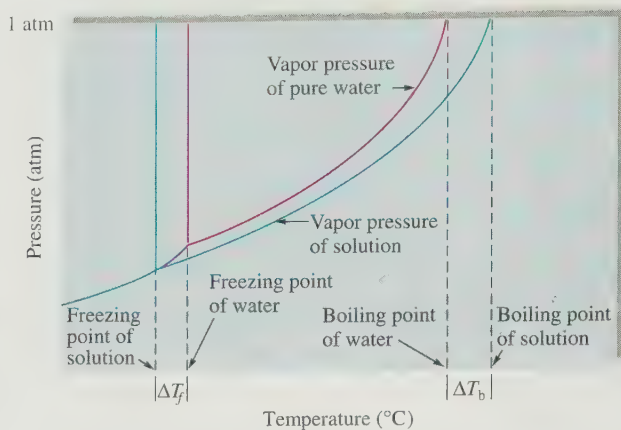
11.5 Boiling-Point Elevation and Freezing-Point Depression

The relationships between vapor pressure and changes of state were discussed in Section 10.8.

In the preceding section we saw how a solute affects the vapor pressure of a liquid solvent. Because changes of state depend on vapor pressure, the presence of a solute also affects the freezing point and boiling point of a solvent. Freezing-point depression, boiling-point elevation, and osmotic pressure (discussed in Section 11.6) are called **colligative properties**. As we will see, they are grouped together because they depend only on the number, and not on the identity, of the solute particles in an ideal solution. Because of their direct relationship to the number of solute particles, the colligative properties are very useful for characterizing the nature of a solute after it is dissolved in a solvent and for determining molar masses of substances.

Boiling-Point Elevation

The normal boiling point of a liquid occurs at the temperature where the vapor pressure is equal to 1 atmosphere. We have seen that a nonvolatile solute lowers the vapor pressure of the solvent. Therefore, such a solution must be heated to a higher temperature than the boiling point of the pure solvent to reach a vapor pressure of

**FIGURE 11.14**

Phase diagrams for pure water (red lines) and for an aqueous solution containing a nonvolatile solute (blue lines). Note that the boiling point of the solution is higher than that of pure water. Conversely, the freezing point of the solution is lower than that of pure water. The effect of a nonvolatile solute is to extend the liquid range of a solvent.

Normal boiling point was defined in Section 10.8.

1 atmosphere. This means that a *nonvolatile solute elevates the boiling point of the solvent*. Figure 11.14 shows the phase diagram for an aqueous solution containing a nonvolatile solute. Note that the liquid/vapor line is shifted to higher temperatures than those for pure water.

As you might expect, the magnitude of the boiling-point elevation depends on the concentration of the solute. The change in boiling point can be represented by the equation

$$\Delta T = K_b m_{\text{solute}}$$

where ΔT is the boiling-point elevation, or the difference between the boiling point of the solution and that of the pure solvent, K_b is a constant that is characteristic of the solvent and is called the **molal boiling-point elevation constant**, and m_{solute} is the *molality* of the solute in the solution.

Values of K_b for some common solvents are given in Table 11.5. The molar mass of a solute can be determined from the observed boiling-point elevation, as shown in Sample Exercise 11.8.

TABLE 11.5 Molal Boiling-Point Elevation Constants (K_b) and Freezing-Point Depression Constants (K_f) for Several Solvents

Solvent	Boiling Point (°C)	K_b (°C · kg/mol)	Freezing Point (°C)	K_f (°C · kg/mol)
Water (H ₂ O)	100.0	0.51	0	1.86
Carbon tetrachloride (CCl ₄)	76.5	5.03	−22.99	30.
Chloroform (CHCl ₃)	61.2	3.63	−63.5	4.70
Benzene (C ₆ H ₆)	80.1	2.53	5.5	5.12
Carbon disulfide (CS ₂)	46.2	2.34	−111.5	3.83
Ethyl ether (C ₄ H ₁₀ O)	34.5	2.02	−116.2	1.79
Camphor (C ₁₀ H ₁₆ O)	208.0	5.95	179.8	40.

SAMPLE EXERCISE 11.8



Sugar dissolved in water to make candy causes the boiling point to be elevated above 100°C.

Calculating the Molar Mass by Boiling-Point Elevation

A solution was prepared by dissolving 18.00 g glucose in 150.0 g water. The resulting solution was found to have a boiling point of 100.34°C. Calculate the molar mass of glucose. Glucose is a molecular solid that is present as individual molecules in solution.

SOLUTION

We make use of the equation

$$\Delta T = K_b m_{\text{solute}}$$

where $\Delta T = 100.34^\circ\text{C} - 100.00^\circ\text{C} = 0.34^\circ\text{C}$

From Table 11.5, for water $K_b = 0.51$. The molality of this solution then can be calculated by rearranging the boiling-point elevation equation to give

$$m_{\text{solute}} = \frac{\Delta T}{K_b} = \frac{0.34^\circ\text{C}}{0.51^\circ\text{C} \cdot \text{kg/mol}} = 0.67 \text{ mol/kg}$$

The solution was prepared using 0.1500 kg water. Using the definition of molality, we can find the number of moles of glucose in the solution.

$$m_{\text{solute}} = 0.67 \text{ mol/kg} = \frac{\text{mol solute}}{\text{kg solvent}} = \frac{n_{\text{glucose}}}{0.1500 \text{ kg}}$$

$$n_{\text{glucose}} = (0.67 \text{ mol/kg})(0.1500 \text{ kg}) = 0.10 \text{ mol}$$

Thus 0.10 mol glucose has a mass of 18.00 g, and 1.0 mol glucose has a mass of 180 g ($10 \times 18.00 \text{ g}$). The molar mass of glucose is 180 g/mol.

See Exercise 11.58.

Melting point and freezing point both refer to the temperature where the solid and liquid coexist.

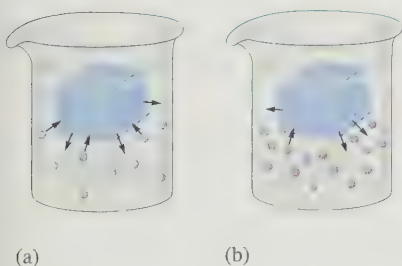


FIGURE 11.15

(a) Ice in equilibrium with liquid water. (b) Ice in equilibrium with liquid water containing a dissolved solute (shown in pink).

Freezing-Point Depression

When a solute is dissolved in a solvent, the freezing point of the solution is lower than that of the pure solvent. Why? Recall that the vapor pressures of ice and liquid water are the same at 0°C. Suppose a solute is dissolved in water. The resulting solution will not freeze at 0°C because *the water in the solution has a lower vapor pressure than that of pure ice*. No ice will form under these conditions. However, the vapor pressure of ice decreases more rapidly than that of liquid water as the temperature decreases. Therefore, as the solution is cooled, the vapor pressure of the ice and that of the liquid water in the solution will eventually become equal. The temperature at which this occurs is the new freezing point of the solution and is below 0°C. The freezing point has been depressed.

We can account for this behavior in terms of the simple model shown in Fig. 11.15. The presence of the solute lowers the rate at which molecules in the liquid return to the solid state. Thus, for an aqueous solution, only the liquid state is found at 0°C. As the solution is cooled, the rate at which water molecules leave the solid ice decreases until this rate and the rate of formation of ice become equal and equilibrium is reached. This is the freezing point of the water in the solution.

Because a solute lowers the freezing point of water, compounds such as sodium chloride and calcium chloride are often spread on streets and sidewalks to prevent



Spreading salt on a highway.

ice from forming in freezing weather. Of course, if the outside temperature is lower than the freezing point of the resulting salt solution, ice forms anyway. So this procedure is not effective at extremely cold temperatures.

The solid/liquid line for an aqueous solution is shown on the phase diagram for water in Fig. 11.14. Since the presence of a solute elevates the boiling point and depresses the freezing point of the solvent, adding a solute has the effect of extending the liquid range.

The equation for freezing-point depression is analogous to that for boiling-point elevation:

$$\Delta T = K_f m_{\text{solute}}$$

where ΔT is the freezing-point depression, or the difference between the freezing point of the pure solvent and that of the solution, and K_f is a constant that is characteristic of a particular solvent and is called the **molal freezing-point depression constant**. Values of K_f for common solvents are listed in Table 11.5.

Like the boiling-point elevation, the observed freezing-point depression can be used to determine molar masses and to characterize solutions.

SAMPLE EXERCISE 11.9



Ethylene glycol.

Freezing-Point Depression

What mass of ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$, molar mass = 62.1 g/mol), the main component of antifreeze, must be added to 10.0 L of water to produce a solution for use in a car's radiator that freezes at -10.0°F (-23.3°C)? Assume the density of water is exactly 1 g/mL.

SOLUTION

The freezing point must be lowered from 0°C to -23.3°C . To determine the molality of ethylene glycol needed to accomplish this, we can use the equation

$$\Delta T = K_f m_{\text{solute}}$$

where $\Delta T = 23.3^\circ\text{C}$ and $K_f = 1.86$ (from Table 11.5). Solving for the molality gives

$$m_{\text{solute}} = \frac{\Delta T}{K_f} = \frac{23.3^\circ\text{C}}{1.86^\circ\text{C} \cdot \text{kg/mol}} = 12.5 \text{ mol/kg}$$

This means that 12.5 mol ethylene glycol must be added per kilogram of water. We have 10.0 L, or 10.0 kg, of water. Therefore, the total number of moles of ethylene glycol needed is

$$\frac{12.5 \text{ mol}}{\text{kg}} \times 10.0 \text{ kg} = 1.25 \times 10^2 \text{ mol}$$

The mass of ethylene glycol needed is

$$1.25 \times 10^2 \text{ mol} \times \frac{62.1 \text{ g}}{\text{mol}} = 7.76 \times 10^3 \text{ g (or 7.76 kg)}$$



The addition of antifreeze lowers the freezing point of water in a car's radiator.

See Exercises 11.61 and 11.62.

SAMPLE EXERCISE 11.10

Determining Molar Mass by Freezing-Point Depression

A chemist is trying to identify a human hormone, which controls metabolism, by determining its molar mass. A sample weighing 0.546 g was dissolved in 15.0 g benzene, and the freezing-point depression was determined to be 0.240°C. Calculate the molar mass of the hormone.

SOLUTION

From Table 11.5, K_f for benzene is 5.12°C · kg/mol, so the molality of the hormone is

$$m_{\text{hormone}} = \frac{\Delta T}{K_f} = \frac{0.240^\circ\text{C}}{5.12^\circ\text{C} \cdot \text{kg/mol}} = 4.69 \times 10^{-2} \text{ mol/kg}$$

The moles of hormone can be obtained from the definition of molality:

$$4.69 \times 10^{-2} \text{ mol/kg} = m_{\text{solute}} = \frac{\text{mol hormone}}{0.0150 \text{ kg benzene}}$$

or

$$\text{mol hormone} = \left(4.69 \times 10^{-2} \frac{\text{mol}}{\text{kg}}\right)(0.0150 \text{ kg}) = 7.04 \times 10^{-4} \text{ mol}$$

Since 0.546 g hormone was dissolved, 7.04 × 10^{−4} mol hormone has a mass of 0.546 g, and

$$\frac{0.546 \text{ g}}{7.04 \times 10^{-4} \text{ mol}} = \frac{x \text{ g}}{1.00 \text{ mol}}$$

$$x = 776 \text{ g/mol}$$

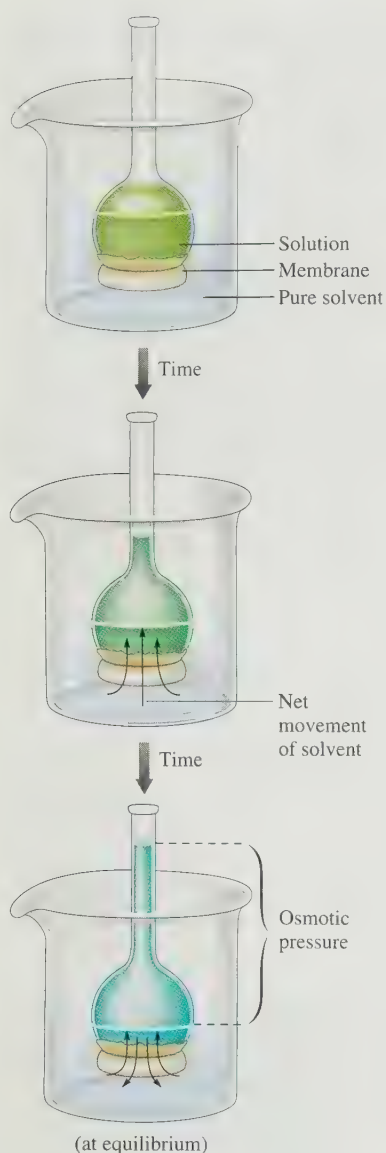
Thus the molar mass of the hormone is 776 g/mol.

See Exercises 11.63 and 11.64.

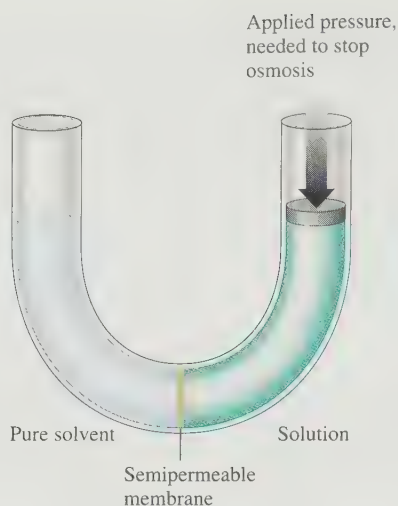
11.6 Osmotic Pressure

Osmotic pressure, another of the colligative properties, can be understood from Fig. 11.16. A solution and pure solvent are separated by a **semipermeable membrane**, which allows *solvent but not solute* molecules to pass through. As time passes, the volume of the solution increases and that of the solvent decreases. This flow of solvent into the solution through the semipermeable membrane is called **osmosis**. Eventually the liquid levels stop changing, indicating that the system has reached equilibrium. Because the liquid levels are different at this point, there is a greater hydrostatic pressure on the solution than on the pure solvent. This excess pressure is called the **osmotic pressure**.

We can take another view of this phenomenon, as illustrated in Fig. 11.17. Osmosis can be prevented by applying a pressure to the solution. *The minimum pressure that stops the osmosis is equal to the osmotic pressure of the solution.* A simple model to explain osmotic pressure can be constructed as shown in Fig. 11.18.

**FIGURE 11.16**

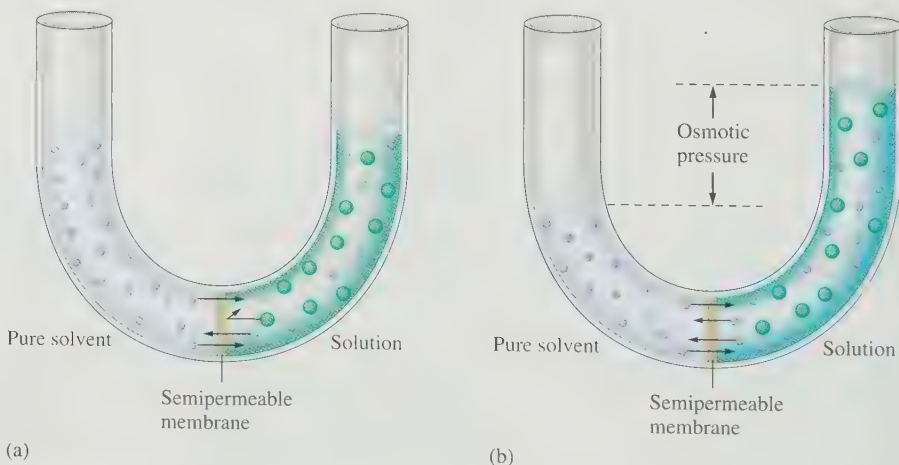
A tube with a bulb on the end that is covered by a semipermeable membrane. The solution is inside the tube and is bathed in the pure solvent. There is a net transfer of solvent molecules into the solution until the hydrostatic pressure equalizes the solvent flow in both directions.

**FIGURE 11.17**

The normal flow of solvent into the solution (osmosis) can be prevented by applying an external pressure to the solution. The minimum pressure required to stop the osmosis is equal to the osmotic pressure of the solution.

The membrane allows only solvent molecules to pass through. However, the initial rates of solvent transfer to and from the solution are not the same. The solute particles interfere with the passage of solvent, so the rate of transfer is slower from the solution to the solvent than in the reverse direction. Thus there is a net transfer of solvent molecules into the solution, which causes the solution volume to increase. As the solution level rises in the tube, the resulting pressure exerts an extra “push” on the solvent molecules in the solution, forcing them back through the membrane. Eventually, enough pressure develops so that the solvent transfer becomes equal in both directions. At this point, equilibrium is achieved and the levels stop changing.

Osmotic pressure can be used to characterize solutions and determine molar masses, as can the other colligative properties, but osmotic pressure is particularly

**FIGURE 11.18**

(a) A pure solvent and its solution (containing a nonvolatile solute) are separated by a semipermeable membrane through which solvent molecules (blue) can pass but solute molecules (green) cannot. The rate of solvent transfer is greater from solvent to solution than from solution to solvent. (b) The system at equilibrium, where the rate of solvent transfer is the same in both directions.

useful because a small concentration of solute produces a relatively large osmotic pressure.

Experiments show that the dependence of the osmotic pressure on solution concentration is represented by the equation

$$\Pi = MRT$$

where Π is the osmotic pressure in atmospheres, M is the molarity of the solution, R is the gas law constant, and T is the Kelvin temperature.

A molar mass determination using osmotic pressure is illustrated in Sample Exercise 11.11.

SAMPLE EXERCISE 11.11

Determining Molar Mass from Osmotic Pressure

To determine the molar mass of a certain protein, 1.00×10^{-3} g of it was dissolved in enough water to make 1.00 mL of solution. The osmotic pressure of this solution was found to be 1.12 torr at 25.0°C. Calculate the molar mass of the protein.

SOLUTION

We use the equation

$$\Pi = MRT$$

In this case we have

$$\Pi = 1.12 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 1.47 \times 10^{-3} \text{ atm}$$

$$R = 0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol}$$

$$T = 25.0 + 273 = 298 \text{ K}$$

Note that the osmotic pressure must be converted to atmospheres because of the units of R .

Solving for M gives

$$M = \frac{1.47 \times 10^{-3} \text{ atm}}{(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(298 \text{ K})} = 6.01 \times 10^{-5} \text{ mol/L}$$

Since 1.00×10^{-3} g protein was dissolved in 1 mL solution, the mass of protein per liter of solution is 1.00 g. The solution's concentration is 6.01×10^{-5} mol/L. This concentration is produced from 1.00×10^{-3} g protein per milliliter, or 1.00 g/L. Thus 6.01×10^{-5} mol protein has a mass of 1.00 g and

$$\frac{1.00 \text{ g}}{6.01 \times 10^{-5} \text{ mol}} = \frac{x \text{ g}}{1.00 \text{ mol}}$$

$$x = 1.66 \times 10^4 \text{ g}$$

The molar mass of the protein is 1.66×10^4 g/mol. This molar mass may seem very large, but it is relatively small for a protein.

See Exercise 11.66.

Measurements of osmotic pressure generally give much more accurate molar mass values than those from freezing-point or boiling-point changes.

In osmosis, a semipermeable membrane prevents transfer of *all* solute particles. A similar phenomenon, called **dialysis**, occurs at the walls of most plant and animal cells. However, in this case the membrane allows transfer of both solvent

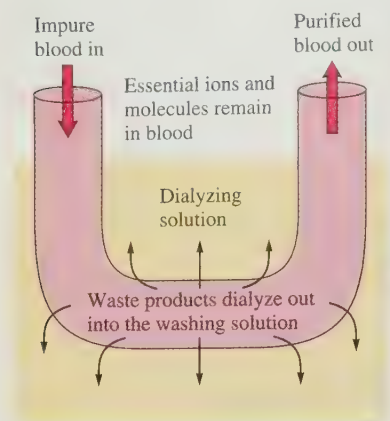
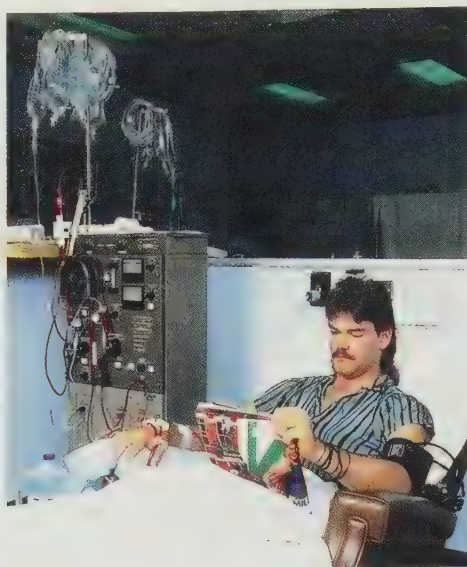


FIGURE 11.19
Representation of the functioning of an artificial kidney.



Patient undergoing dialysis.

molecules and *small* solute molecules and ions. One of the most important applications of dialysis is the use of artificial kidney machines to purify the blood. The blood is passed through a cellophane tube, which acts as the semipermeable membrane. The tube is immersed in a dialyzing solution (see Fig. 11.19). This “washing” solution contains the same concentrations of ions and small molecules as blood but has none of the waste products normally removed by the kidneys. The resulting dialysis (movement of waste molecules into the washing solution) cleanses the blood.

Solutions that have identical osmotic pressures are said to be **isotonic solutions**. Fluids administered intravenously must be isotonic with body fluids. For example, if red blood cells are bathed in a hypertonic solution, which is a solution having an osmotic pressure higher than that of the cell fluids, the cells will shrivel because of a net transfer of water out of the cells. This phenomenon is called *crenation*. The opposite phenomenon, called *hemolysis*, occurs when cells are bathed in a hypotonic solution, a solution with an osmotic pressure lower than that of the cell fluids. In this case, the cells rupture because of the flow of water into the cells.

We can use the phenomenon of crenation to our advantage. Food can be preserved by treating its surface with a solute that gives a solution that is hypertonic to bacteria cells. Bacteria on the food then tend to shrivel and die. This is why salt can be used to protect meat and sugar can be used to protect fruit.

The brine used in pickling causes the cucumbers to shrivel.

SAMPLE EXERCISE 11.12

Isotonic Solutions

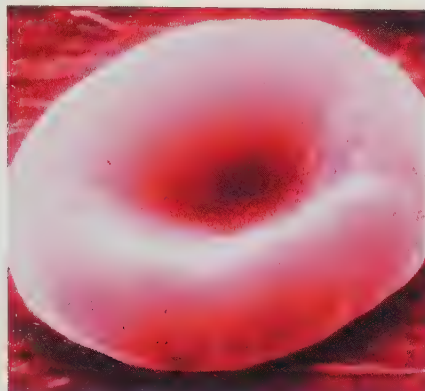
What concentration of sodium chloride in water is needed to produce an aqueous solution isotonic with blood ($\Pi = 7.70$ atm at 25°C)?

SOLUTION

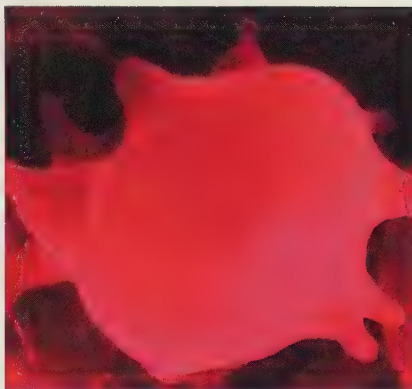
We can calculate the molarity of the solute from the equation

$$\Pi = MRT \quad \text{or} \quad M = \frac{\Pi}{RT}$$

$$M = \frac{7.70 \text{ atm}}{(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(298 \text{ K})} = 0.315 \text{ mol/L}$$



(a)



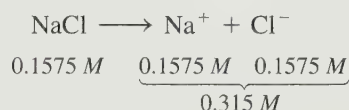
(b)



(c)

Red blood cells in three stages of osmosis. (a) The normal shape of a red blood cell. (b) This cell has shrunk because water moved out of it by osmosis. (c) This cell is swollen with water that has moved into it by osmosis.

This represents the total molarity of solute particles. But NaCl gives two ions per formula unit. Therefore, the concentration of NaCl needed is $\frac{0.315 M}{2} = 0.1575 M = 0.158 M$. That is,



See Exercise 11.68.

Reverse Osmosis

If a solution in contact with pure solvent across a semipermeable membrane is subjected to an external pressure larger than its osmotic pressure, **reverse osmosis** occurs. The pressure will cause a net flow of solvent from the solution to the solvent, as shown in Fig. 11.20. In reverse osmosis, the semipermeable membrane acts as a “molecular filter” to remove solute particles. This fact is applicable to the **desalination** (removal of dissolved salts) of seawater, which is highly hypertonic to body fluids and thus is not drinkable.

As the population of the Sun Belt areas of the United States increases, more demand will be placed on the limited supplies of fresh water there. One obvious source of fresh water is from the desalination of seawater. Various schemes have been suggested, including solar evaporation, reverse osmosis, and even a plan for towing icebergs from Antarctica. The problem, of course, is that all the available processes are expensive. However, as water shortages increase, desalination is becoming necessary. For example, the first full-time public desalination plant in the United States started operations on Catalina Island, just off the coast of California (see Fig. 11.21). This plant, which can produce 132,000 gallons of drinkable water from the Pacific Ocean every day, operates by reverse osmosis. Powerful pumps, developing over 800 lb/in² of pressure, are employed to force seawater through synthetic semipermeable membranes.

Catalina Island’s plant may be just the beginning. The city of Santa Barbara opened a \$40 million desalination plant in 1992 that can produce 8 million gallons of drinking water per day, and other plants are in the planning stages.

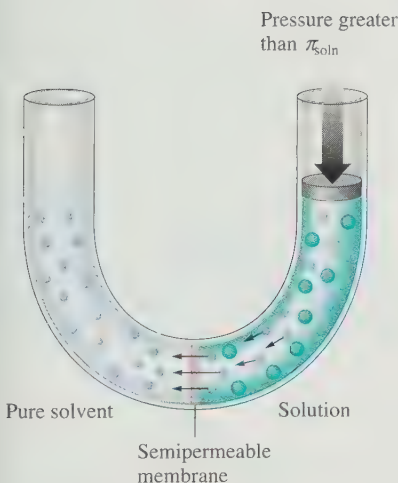
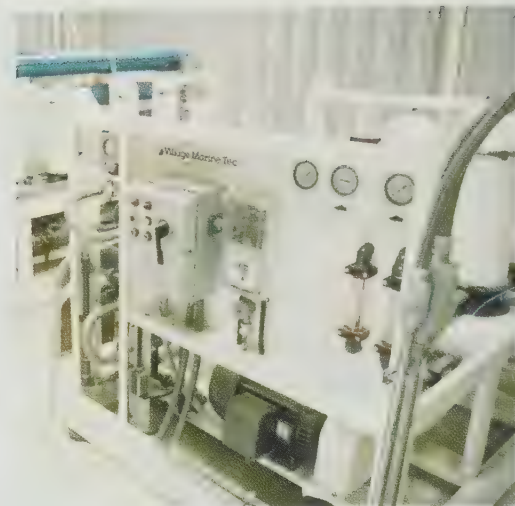
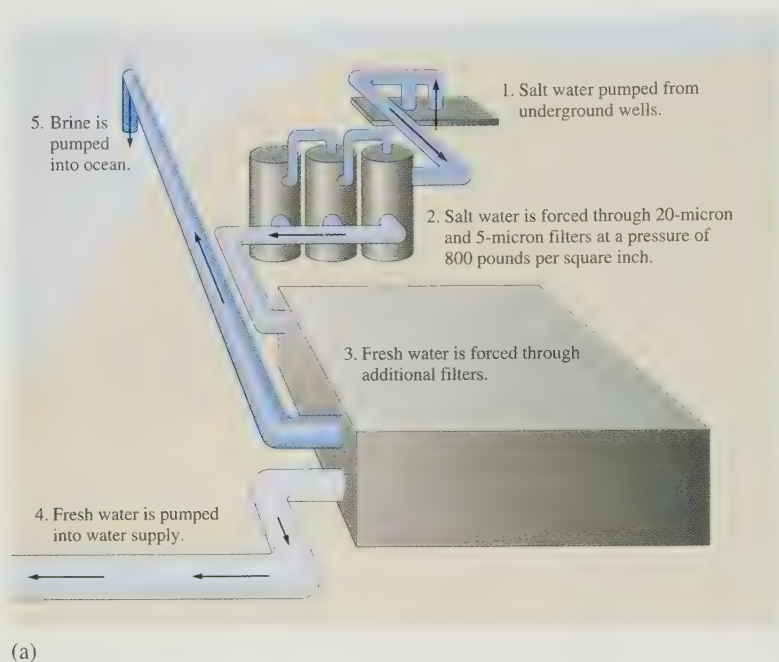


FIGURE 11.20

Reverse osmosis. A pressure greater than the osmotic pressure of the solution is applied, which causes a net flow of solvent molecules (blue) from the solution to the pure solvent. The solute molecules (green) remain behind.

**FIGURE 11.21**

(a) Residents of Catalina Island off the coast of southern California are benefiting from a new desalination plant that can supply 132,000 gallons a day, or one-third of the island's daily needs. (b) Machinery in the desalination plant for Catalina Island.

A small-scale, manually operated reverse osmosis desalinators have been developed by the U.S. Navy to provide fresh water on life rafts. Potable water can be supplied by this desalinator at the rate of 1.25 gallons of water per hour—enough to keep 25 people alive. This compact desalinator, which weighs only 10 pounds, can now replace the bulky cases of fresh water formerly stored in Navy life rafts.

11.7 Colligative Properties of Electrolyte Solutions

As we have seen previously, the colligative properties of solutions depend on the total concentration of solute particles. For example, a 0.10 *m* glucose solution shows a freezing-point depression of 0.186°C:

$$\Delta T = K_f m = (1.86^\circ\text{C} \cdot \text{kg/mol})(0.100 \text{ mol/kg}) = 0.186^\circ\text{C}$$

On the other hand, a 0.10 *m* sodium chloride solution should show a freezing-point depression of 0.37°C, since the solution is 0.10 *m* Na⁺ ions and 0.10 *m* Cl⁻ ions. Therefore, the solution contains a total of 0.20 *m* solute particles, and $\Delta T = (1.86^\circ\text{C} \cdot \text{kg/mol})(0.20 \text{ mol/kg}) = 0.37^\circ\text{C}$.

The relationship between the moles of solute dissolved and the moles of particles in solution is usually expressed using the **van't Hoff factor**, *i*:

$$i = \frac{\text{moles of particles in solution}}{\text{moles of solute dissolved}}$$

Dutch chemist J. H. van't Hoff (1852–1911) received the first Nobel Prize in chemistry in 1901.

CHEMICAL IMPACT

The Drink of Champions—Water

In 1965, the University of Florida football team, the Gators, participated in a research program to test a sports drink formula containing a mixture of carbohydrates and electrolytes. The drink was used to help prevent dehydration caused by extreme workouts in the hot Florida climate. The Gators' success that season was in part attributed to their use of the sports drink formula. In 1967, a modified form of this formula was marketed with the name Gatorade. Today, Gatorade leads sales in sports drinks, but many other brands have entered a market where annual sales exceed \$700 million!

During moderate- to high-intensity exercise, glycogen (a fuel reserve that helps maintain normal body processes) can be depleted within 60 to 90 minutes. Blood sugar levels drop as the glycogen reserves are used up, and lactic acid (a by-product of glucose metabolism) builds up in muscle tissue causing fatigue and muscle cramps. Muscles also generate a large amount of heat that must be dissipated. Water, which has a large specific heat capacity, is used to take heat away from these muscles. Sweating and evaporative cooling help the body maintain a constant temperature, but at a huge cost. During a high-intensity workout in hot weather, anywhere from 1 to 3 quarts of water can be lost from sweating per hour. Sweating away more than 2% of your body weight—a quart for every 100 pounds—can put a large stress on the heart, increasing body temperature and decreasing performance. Excessive sweating also results in the loss of sodium and potassium ions—two very important electrolytes that are present in the fluids inside and outside cells.

All the major sports drinks contain three main ingredients—carbohydrates in the form of simple sugars such as sucrose, glucose, and fructose; electrolytes, including sodium and potassium ions; and water. Because these are the three major substances lost through sweating, good scientific reasoning suggests that drinking sports drinks should



For healthy athletes, drinking water during exercise may be as effective as drinking sports drinks.

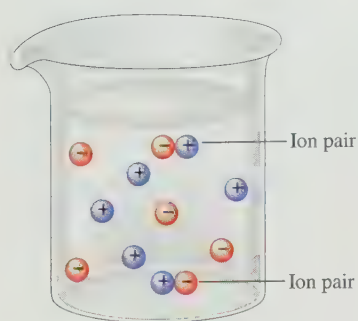
improve performance. But just how effectively do sports drinks deliver on their promises?

Recent studies have confirmed that athletes who eat a balanced diet and drink plenty of water are just as well off as those who consume sports drinks. A sports drink may have only one advantage over drinking water—it tastes better than water to most athletes. And if a drink tastes better, it will encourage more consumption, thus keeping cells hydrated.

Since most of the leading sports drinks contain the same ingredients in similar concentrations, taste may be the single most important factor in choosing your drink. If you are not interested in any particular sports drink, drink plenty of water. The key to quality performance is to keep your cells hydrated.

Adapted with permission from "Sports Drinks: Don't Sweat the Small Stuff," by Tim Graham, *ChemMatters*, February 1999, p. 11.

The *expected* value for i can be calculated for a salt by noting the number of ions per formula unit. For example, for NaCl , i is 2; for K_2SO_4 , i is 3; and for $\text{Fe}_3(\text{PO}_4)_2$, i is 5. These calculated values assume that when a salt dissolves, it completely dissociates into its component ions, which then move around independently. This assumption is not always true. For example, the freezing-point depression observed for 0.10 m NaCl is 1.87 times that for 0.10 m glucose rather than twice as great. That is, for a 0.10 m NaCl solution the observed value for i is 1.87 rather

**FIGURE 11.22**

In an aqueous solution a few ions aggregate, forming ion pairs that behave as a unit.

TABLE 11.6 Expected and Observed Values of the van't Hoff Factor for 0.05 *m* Solutions of Several Electrolytes

Electrolyte	<i>i</i> (expected)	<i>i</i> (observed)
NaCl	2.0	1.9
MgCl ₂	3.0	2.7
MgSO ₄	2.0	1.3
FeCl ₃	4.0	3.4
HCl	2.0	1.9
Glucose*	1.0	1.0

*A nonelectrolyte shown for comparison.

than 2. Why? The best explanation is that **ion pairing** occurs in solution (see Fig. 11.22). At a given instant a small percentage of the sodium and chloride ions are paired and thus count as a single particle. In general, ion pairing is most important in concentrated solutions. As the solution becomes more dilute, the ions are farther apart and less ion pairing occurs. For example, in a 0.0010 *m* NaCl solution, the observed value of *i* is 1.97, which is very close to the expected value.

Ion pairing occurs to some extent in all electrolyte solutions. Table 11.6 shows expected and observed values of *i* for a given concentration of various electrolytes. Note that the deviation of *i* from the expected value tends to be greatest where the ions have multiple charges. This is expected because ion pairing ought to be most important for highly charged ions.

The colligative properties of electrolyte solutions are described by including the van't Hoff factor in the appropriate equation. For example, for changes in freezing and boiling points, the modified equation is

$$\Delta T = imK$$

where *K* represents the freezing-point depression or boiling-point elevation constant for the solvent.

For the osmotic pressure of electrolyte solutions, the equation is

$$\Pi = iMRT$$

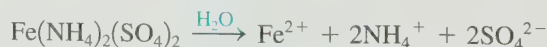
SAMPLE EXERCISE 11.13

Osmotic Pressure

The observed osmotic pressure for a 0.10 *M* solution of Fe(NH₄)₂(SO₄)₂ at 25°C is 10.8 atm. Compare the expected and experimental values for *i*.

SOLUTION

The ionic solid Fe(NH₄)₂(SO₄)₂ dissociates in water to produce 5 ions:



Thus the expected value for *i* is 5. We can obtain the experimental value for *i* by using the equation for osmotic pressure:

$$\Pi = iMRT \quad \text{or} \quad i = \frac{\Pi}{MRT}$$

where $\Pi = 10.8 \text{ atm}$, $M = 0.10 \text{ mol/L}$, $R = 0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol}$, and $T = 25 + 273 = 298 \text{ K}$. Substituting these values into the equation gives

$$i = \frac{\Pi}{MRT} = \frac{10.8 \text{ atm}}{(0.10 \text{ mol/L})(0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(298 \text{ K})} = 4.4$$

The experimental value for i is less than the expected value, presumably because of ion pairing.

See Exercises 11.73 through 11.75.

11.8 Colloids

Mud can be suspended in water by vigorous stirring. When the stirring stops, most of the particles rapidly settle out, but even after several days some of the smallest particles remain suspended. Although undetected in normal lighting, their presence can be demonstrated by shining a beam of intense light through the suspension. The beam is visible from the side because the light is scattered by the suspended particles (Fig. 11.23). In a true solution, on the other hand, the beam is invisible from the side because the individual ions and molecules dispersed in the solution are too small to scatter visible light.

The scattering of light by particles is called the **Tyndall effect** and is often used to distinguish between a suspension and a true solution.

A suspension of tiny particles in some medium is called a **colloidal dispersion**, or a **colloid**. The suspended particles are single large molecules or aggregates of molecules or ions ranging in size from 1 to 1000 nm. Colloids are classified according to the states of the dispersed phase and the dispersing medium. Table 11.7 summarizes various types of colloids.

What stabilizes a colloid? Why do the particles remain suspended rather than forming larger aggregates and precipitating out? The answer is complicated, but the main factor seems to be *electrostatic repulsion*. A colloid, like all other macroscopic substances, is electrically neutral. However, when a colloid is placed in an electric field, the dispersed particles all migrate to the same electrode and thus must all have the same charge. How is this possible? The center of a colloidal particle (a tiny ionic crystal, a group of molecules, or a single large molecule) attracts from the medium a layer of ions, all of the same charge. This group of ions, in turn, attracts another



FIGURE 11.23
The Tyndall effect.

TABLE 11.7 Types of Colloids

Examples	Dispersing Medium	Dispersed Substance	Colloid Type
Fog, aerosol sprays	Gas	Liquid	Aerosol
Smoke, airborne bacteria	Gas	Solid	Aerosol
Whipped cream, soap suds	Liquid	Gas	Foam
Milk, mayonnaise	Liquid	Liquid	Emulsion
Paint, clays, gelatin	Liquid	Solid	Sol
Marshmallow, polystyrene foam	Solid	Gas	Solid foam
Butter, cheese	Solid	Liquid	Solid emulsion
Ruby glass	Solid	Solid	Solid sol

CHEMICAL IMPACT

Organisms and Ice Formation

The ice-cold waters of the polar oceans are teeming with fish that seem immune to freezing. One might think that these fish have some kind of antifreeze in their blood. However, studies show that they are protected from freezing in a very different way from the way antifreeze protects our cars. As we have seen in this chapter, solutes such as sugar, salt, and ethylene glycol lower the temperature at which the solid and liquid phases of water can coexist. However, the fish could not tolerate high concentrations of solutes in their blood because of the osmotic pressure effects. Instead, they are protected by proteins in their blood. These proteins allow the water in the bloodstream to be supercooled—exist below 0°C —without forming ice. They apparently coat the surface of each tiny ice crystal, as soon as it begins to form, preventing it from growing to a size that would cause biologic damage.

Although it might at first seem surprising, this research on polar fish has attracted the attention of ice cream manufacturers. Premium quality ice cream is smooth; it does not have large ice crystals in it. The makers of ice cream would like to incorporate these polar fish proteins, or molecules that behave similarly, into ice cream to prevent the growth of ice crystals during storage.

Fruit and vegetable growers have a similar interest: They also want to prevent ice formation that damages their crops during an unusual cold wave. However, this is a very different kind of problem than keeping polar fish from freezing. Many types of fruits and vegetables are colonized by bacteria that manufacture a protein that *encourages* freezing



An Antarctic fish, *Chaerophalus aceratus*.

by acting as a nucleating agent to start an ice crystal. Chemists have identified the offending protein in the bacteria and the gene that is responsible for making it. They have learned to modify the genetic material of these bacteria in a way that removes their ability to make the protein that encourages ice crystal formation. If testing shows that these modified bacteria have no harmful effects on the crop or the environment, the original bacteria strain will be replaced with the new form so that ice crystals will not form so readily when a cold snap occurs.

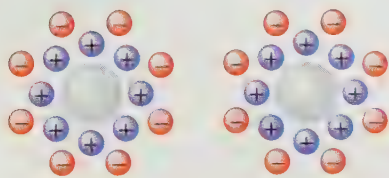


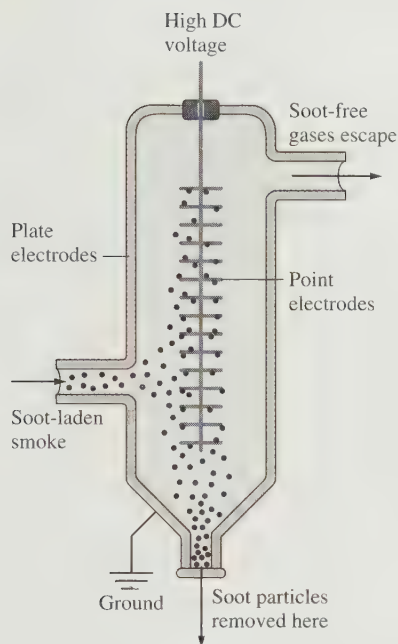
FIGURE 11.24

A representation of two colloidal particles. In each the center particle is surrounded by a layer of positive ions, with negative ions in the outer layer. Thus, although the particles are electrically neutral, they still repel each other because of their outer negative layer of ions.

layer of oppositely charged ions, as shown in Fig. 11.24. Because the colloidal particles all have an outer layer of ions with the same charge, they repel each other and do not easily aggregate to form particles that are large enough to precipitate.

The destruction of a colloid, called **coagulation**, usually can be accomplished either by heating or by adding an electrolyte. Heating increases the velocities of the colloidal particles, causing them to collide with enough energy that the ion barriers are penetrated and the particles can aggregate. Because this process is repeated many times, the particle grows to a point where it settles out. Adding an electrolyte neutralizes the adsorbed ion layers. This is why clay suspended in rivers is deposited where the river reaches the ocean, forming the deltas characteristic of large rivers like the Mississippi. The high salt content of the seawater causes the colloidal clay particles to coagulate.

The removal of soot from smoke is another example of the coagulation of a colloid. When smoke is passed through an electrostatic precipitator (Fig. 11.25), the suspended solids are removed. The use of precipitators has produced an immense improvement in the air quality of heavily industrialized cities.

**FIGURE 11.25**

The Cottrell precipitator installed in a smokestack. The charged plates attract the colloidal particles because of their ion layers and thus remove them from the smoke.

For Review

Summary

Solution composition can be described in terms of molarity (the moles of solute per liter of solution), mass percent (the ratio of grams of solute to grams of solution multiplied by 100), mole fraction (the moles of a given component per total number of moles of all components of the solution), or molality (the moles of solute per kilogram of solvent).

Normality is defined as the number of equivalents per liter of solution. The definition of an equivalent depends on the reaction taking place in the solution. For an acid–base reaction, the equivalent is the mass of acid (or base) that can furnish (or accept) exactly 1 mole of protons. For an oxidation–reduction reaction, the equivalent is the quantity of reducing (or oxidizing) agent that can furnish (or accept) 1 mole of electrons.

The enthalpy of solution ΔH_{soln} is the enthalpy change accompanying solution formation. It can be broken down into terms expressing energies associated with overcoming interactions between solute particles and interactions between solvent particles (endothermic processes) and a term expressing energies associated with the interactions between solute and solvent particles (an exothermic process).

Various factors affect solubility. Molecular structure determines the polarity of a molecule. Polar molecules tend to be soluble in polar solvents, and nonpolar molecules tend to be soluble in nonpolar solvents. Pressure has little effect on the solubility of liquids or solids, but increased pressure increases the solubility of gases. Henry's law, which applies to gases that do not react chemically with the solvent, states that the concentration of a gaseous solute in a solvent is directly proportional to the partial pressure of the same gas above the solution. An increase in temperature decreases the solubility of a gas in water, but the effect of temperature on the solubility of a solid in water varies with the identity of the solid.

Key Terms

Section 11.1

molarity
mass percent
mole fraction
molality
normality

Section 11.2

enthalpy (heat) of solution
enthalpy (heat) of hydration

Section 11.3

Henry's law
thermal pollution

Section 11.4

Raoult's law
ideal solution

Section 11.5

colligative properties
molal boiling-point elevation
constant
molal freezing-point depression
constant

Section 11.6

semipermeable membrane
osmosis
osmotic pressure
dialysis
isotonic solution
reverse osmosis
desalination

Section 11.7

van't Hoff factor
ion pairing

Section 11.8

Tyndall effect
colloid (colloidal dispersion)
coagulation

The vapor pressure of a solution containing a nonvolatile solute is always less than the vapor pressure of the pure solvent, because the presence of the solute decreases the number of solvent molecules per unit volume and thus proportionately lowers the escaping tendency of the solvent molecules. Raoult's law states that the vapor pressure of a solution is directly proportional to the mole fraction of the solvent. Raoult's law holds for an ideal solution. However, if a solute has a special affinity for the solvent, nonideal behavior is seen in the form of a negative deviation from Raoult's law (a lower vapor pressure than is predicted).

The colligative properties of solutions, which depend on the number of solute particles present, include boiling-point elevation, freezing-point depression, and osmotic pressure. Because a nonvolatile solute lowers the freezing point and raises the boiling point, it extends the liquid range of the solvent.

Osmosis occurs when a pure solvent and its solution are separated by a semipermeable membrane that prevents the passage of solute molecules. Under these circumstances, solvent molecules flow from the solvent into the solution. Osmotic pressure, the exact pressure that must be applied to a solution to prevent osmosis, is directly related to the molarity of the solution. Reverse osmosis occurs when an external pressure larger than the solution's osmotic pressure is applied. The effect is to cause a net flow of solvent from the solution into the pure solvent.

To describe the colligative properties of electrolyte solutions, the number of ions must be taken into account by use of the van't Hoff factor i . Because of ion pairing, the experimental value for i is often significantly less than the expected value.

A colloid is a suspension of tiny particles in solution. Colloids are stabilized because of the electrostatic repulsions between the ion layers surrounding the individual particles. A colloid can be coagulated by heating or by adding an electrolyte.

In-Class Discussion Questions

These questions are designed to be considered by groups of students in class. Often these questions work well for introducing a particular topic in class.

- Consider Fig. 11.9. According to the caption and picture, water seems to go from one beaker to another.
 - Explain why this occurs.
 - The explanation in the text uses terms such as *vapor pressure* and *equilibrium*. Explain what these have to do with the phenomenon. For example, what is coming to equilibrium?
 - Does all the water end up in the second beaker?
 - Is water evaporating from the beaker containing the solution? If so, is the rate of evaporation increasing, decreasing, or staying constant?

Draw pictures to illustrate your explanations.

- Once again, consider Fig. 11.9. Suppose instead of having a nonvolatile solute in the solvent in one beaker, the two beakers contain different volatile liquids. That is, suppose one beaker contains liquid A ($P_{\text{vap}} = 50$ torr) and the other beaker contains liquid B ($P_{\text{vap}} = 100$ torr). Explain what happens as time

passes. How is this similar to the first case (shown in the figure)? How is it different?

- Assume that you place a freshwater plant into a saltwater solution and examine it under a microscope. What happens to the plant cells? What if you placed a saltwater plant in pure water? Explain. Draw pictures to illustrate your explanations.
- How does ΔH_{soln} relate to deviations from Raoult's law? Explain.
- You have read that adding a solute to a solvent can both increase the boiling point and decrease the freezing point. A friend of yours explains it to you like this: "The solute and solvent can be like salt in water. The salt gets in the way of freezing in that it blocks the water molecules from joining together. The salt acts like a strong bond holding the water molecules together so that it is harder to boil." What do you say to your friend?
- You drop an ice cube (made from pure water) into a saltwater solution at 0°C . Explain what happens and why.
- Using the phase diagram for water and Raoult's law, explain why salt is spread on the roads in winter (even when it is below freezing).
- You and your friend are each drinking cola from separate 2-L bottles. Both colas are equally carbonated. You are able to

drink 1 L of cola, but your friend can drink only about half a liter. You each close the bottles and place them in the refrigerator. The next day when you each go to get the colas, whose will be more carbonated and why?

A blue question or exercise number indicates that the answer to that question or exercise appears at the back of this book and a solution appears in the *Solutions Guide*.

Solution Review

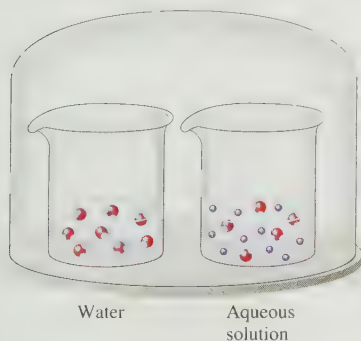
If you have trouble with these exercises, review Sections 4.1 to 4.3 in Chapter 4.

9. A solution is prepared by dissolving 125 g sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) in enough water to produce 1.00 L solution. What is the molarity of this solution?
10. What mass of sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$) is needed to prepare 0.250 L of a 0.100 M solution?
11. A solution is prepared by diluting 25.00 mL of a 0.308 M solution of NiCl_2 to a final volume of 0.500 L. What is the concentration of nickel chloride in this solution? What are the concentrations of nickel ions and chloride ions in this solution?
12. Write equations showing the ions present after the following strong electrolytes are dissolved in water.

a. HNO_3	d. SrBr_2	g. NH_4NO_3
b. Na_2SO_4	e. KClO_4	h. CuSO_4
c. $\text{Al}(\text{NO}_3)_3$	f. NH_4Br	i. NaOH

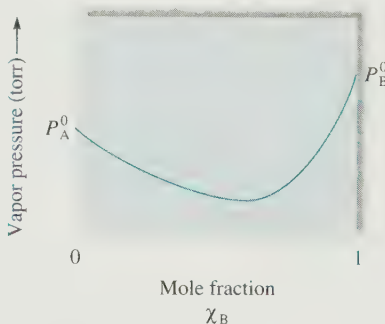
Questions

13. Is molarity or molality dependent on temperature? Explain your answer. Why is molality, and not molarity, used in the equations describing freezing-point depression and boiling-point elevation?
14. What specific feature of chemical substances do we refer to when we say that “like dissolves like”?
15. Define the terms *hydrophobic* and *hydrophilic*.
16. Rationalize the temperature dependence of the solubility of a gas in water in terms of the kinetic molecular theory.
17. The two beakers in the sealed container illustrated below contain pure water and an aqueous solution of a volatile solute.



If the solute is less volatile than water, explain what will happen to the volumes in the two containers as time passes.

18. The following plot shows the vapor pressure of various solutions of components A and B at some temperature.



Which of the following statements is false concerning solutions of A and B?

- a. The solutions exhibit negative deviations from Raoult's law.
 - b. ΔH_{mix} for the solutions should be exothermic.
 - c. The intermolecular forces are stronger in solution than in either pure A or pure B.
 - d. Pure liquid B is more volatile than pure liquid A.
 - e. The solution with $\chi_B = 0.6$ will have a lower boiling point than either pure A or pure B.
19. When pure methanol is mixed with water, the resulting solution feels warm. Would you expect this solution to be ideal? Explain.
 20. Why is the observed freezing-point depression for electrolyte solutions sometimes less than the calculated value? Is the discrepancy greater for concentrated or dilute solutions?
 21. Before refrigeration was common, many foods were preserved by salting them heavily, and many fruits were preserved by mixing them with a large amount of sugar (fruit preserves). How do salt and sugar act as preservatives?
 22. Distinguish between a strong electrolyte and a weak electrolyte. How can colligative properties be used to distinguish between strong and weak electrolytes?
 23. The Tyndall effect is often used to distinguish between a colloidal suspension and a true solution. Explain.
 24. Detergent molecules can stabilize the emulsion of oil in water as well as remove dirt from soiled clothes. A typical detergent is sodium dodecylsulfate, or SDS, and it has a formula of $\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{SO}_4^-\text{Na}^+$. In aqueous solution, SDS suspends oil or dirt by forming small aggregates of detergent anions called *micelles*. Propose a structure for micelles.

Exercises

In this section similar exercises are paired.

Concentration of Solutions

25. A solution is made by dissolving 25 g of NaCl in enough water to make 1.00 L of solution. Assume that the density of the solution is 1.00 g/cm³. Calculate the mass percent, molarity, molality, and mole fraction of NaCl.
26. An aqueous antifreeze solution is 40.0% ethylene glycol (C₂H₆O₂) by mass. The density of the solution is 1.05 g/cm³. Calculate the molality, molarity, and mole fraction of the ethylene glycol.
27. Common commercial acids and bases are aqueous solutions with the following properties:

	Density (g/cm ³)	Mass Percent of Solute
Hydrochloric acid	1.19	38
Nitric acid	1.42	70
Sulfuric acid	1.84	95
Acetic acid	1.05	99
Ammonia	0.90	28

Calculate the molarity, molality, and mole fraction of each of the preceding reagents.

28. In lab you need to prepare at least 100 mL of each of the following solutions. Explain how you would proceed using the given information.
- 2.0 *m* KCl in water (density of H₂O = 1.00 g/cm³)
 - 15% NaOH by mass in water (*d* = 1.00 g/cm³)
 - 25% NaOH by mass in CH₃OH (*d* = 0.79 g/cm³)
 - 0.10 mole fraction of C₆H₁₂O₆ in water (*d* = 1.00 g/cm³)
29. A solution is prepared by mixing 25 mL pentane (C₅H₁₂, *d* = 0.63 g/cm³) with 45 mL hexane (C₆H₁₄, *d* = 0.66 g/cm³). Assuming that the volumes add on mixing, calculate the mass percent, mole fraction, molality, and molarity of the pentane.
30. A bottle of wine contains 12.5% ethanol by volume. The density of ethanol (C₂H₅OH) is 0.789 g/cm³. Calculate the concentration of ethanol in wine in terms of mass percent and molality.
31. A 1.37 *M* solution of citric acid (H₃C₆H₅O₇) in water has a density of 1.10 g/cm³. Calculate the mass percent, molality, mole fraction, and normality of the citric acid. Citric acid has three acidic protons.
32. Calculate the molarity and mole fraction of acetone in a 1.00 *m* solution of acetone (CH₃COCH₃) in ethanol (C₂H₅OH). (Density of acetone = 0.788 g/cm³; density of ethanol = 0.789 g/cm³.) Assume that the volumes of acetone and ethanol add.

Energetics of Solutions and Solubility

33. The lattice energy* of NaI is -686 kJ/mol, and the enthalpy of hydration is -694 kJ/mol. Calculate the enthalpy of solution per mole of solid NaI. Describe the process to which this enthalpy change applies.
34. a. Use the following data to calculate the enthalpy of hydration for calcium chloride and calcium iodide.

	Lattice Energy*	ΔH_{soln}
CaCl ₂ (s)	-2247 kJ/mol	-46 kJ/mol
CaI ₂ (s)	-2059 kJ/mol	-104 kJ/mol

- b. Based on your answers to part a, which ion, Cl⁻ or I⁻, is more strongly attracted to water?

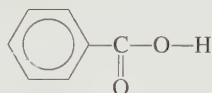
35. Although Al(OH)₃ is insoluble in water, NaOH is very soluble. Explain in terms of lattice energies.*
36. The high melting points of ionic solids indicate that a lot of energy must be supplied to separate the ions from one another. How is it possible that the ions can separate from one another when soluble ionic compounds are dissolved in water, often with essentially no temperature change?
37. Which solvent, water or carbon tetrachloride, would you choose to dissolve each of the following?
- CO₂
 - NH₄NO₃
 - CH₃CCH₃
 $\begin{array}{c} \text{O} \\ \parallel \\ \text{C} \end{array}$
 - HC₂H₃O₂
 - CH₃CH₂CH₂CH₂CH₃
 - (NH₄)₂SO₄
38. Which solvent, water or hexane (C₆H₁₄), would you choose to dissolve each of the following?
- NaCl
 - HF
 - octane (C₈H₁₈)
 - (NH₄)₂SO₄
39. What factors cause one solute to be more strongly attracted to water than another? For each of the following pairs, predict which substance would be more soluble in water.
- CH₃CH₂OH or CH₃CH₂CH₃
 - CHCl₃ or CCl₄
 - CH₃CH₂OH or CH₃(CH₂)₁₄CH₂OH
40. Which ion in each of the following pairs would you expect to be more strongly hydrated? Why?
- Na⁺ or Mg²⁺
 - Mg²⁺ or Be²⁺
 - Fe²⁺ or Fe³⁺
 - F⁻ or Br⁻
 - Cl⁻ or ClO₄⁻
 - ClO₄⁻ or SO₄²⁻

* Lattice energy was defined in Chapter 8 as the energy change for the process $M^+(g) + X^-(g) \rightarrow MX(s)$.

41. Rationalize the trend in water solubility for the following simple alcohols:

Alcohol	Solubility (g/100 g H ₂ O at 20°C)
Methanol, CH ₃ OH	Soluble in all proportions
Ethanol, CH ₃ CH ₂ OH	Soluble in all proportions
Propanol, CH ₃ CH ₂ CH ₂ OH	Soluble in all proportions
Butanol, CH ₃ (CH ₂) ₂ CH ₂ OH	8.14
Pentanol, CH ₃ (CH ₂) ₃ CH ₂ OH	2.64
Hexanol, CH ₃ (CH ₂) ₄ CH ₂ OH	0.59
Heptanol, CH ₃ (CH ₂) ₅ CH ₂ OH	0.09

42. The solubility of benzoic acid (HC₇H₅O₂),



is 0.34 g/100 mL in water at 25°C and is 10.0 g/100 mL in benzene (C₆H₆) at 25°C. Rationalize this solubility behavior. (*Hint:* Benzoic acid forms a dimer in benzene.) Would benzoic acid be more or less soluble in a 0.1 M NaOH solution than it is in water? Explain.

43. The solubility of nitrogen in water is 8.21×10^{-4} mol/L at 0°C when the N₂ pressure above water is 0.790 atm. Calculate the Henry's law constant for N₂ in units of mol/L · atm for Henry's law in the form $C = kP$, where C is the gas concentration in mol/L. Calculate the solubility of N₂ in water when the partial pressure of nitrogen above water is 1.10 atm at 0°C.
44. In Exercise 103 in Chapter 5, the pressure of CO₂ in a bottle of sparkling wine was calculated assuming that the CO₂ was insoluble in water. This was a bad assumption. Redo this problem by assuming that CO₂ obeys Henry's law. Use the data given in that problem to calculate the partial pressure of CO₂ in the gas phase and the solubility of CO₂ in the wine at 25°C. The Henry's law constant for CO₂ is 3.1×10^{-2} mol/L · atm at 25°C with Henry's law in the form $C = kP$, where C is the concentration of the gas in mol/L.

Vapor Pressures of Solutions

45. A solution is prepared by mixing 50.0 g glucose (C₆H₁₂O₆) with 600.0 g water. What is the vapor pressure of this solution at 25°C? (At 25°C the vapor pressure of pure water is 23.8 torr. Glucose is a nonelectrolyte.)
46. The vapor pressure of a solution containing 53.6 g glycerin

(C₃H₈O₃) in 133.7 g ethanol (C₂H₅OH) is 113 torr at 40°C. Calculate the vapor pressure of pure ethanol at 40°C assuming that glycerin is a nonvolatile, nonelectrolyte solute in ethanol.

47. At a certain temperature, the vapor pressure of pure benzene (C₆H₆) is 0.930 atm. A solution was prepared by dissolving 10.0 g of a nondissociating, nonvolatile solute in 78.11 g of benzene at that temperature. The vapor pressure of the solution was found to be 0.900 atm. Assuming the solution behaves ideally, determine the molar mass of the solute.
48. A solution of sodium chloride in water has a vapor pressure of 19.6 torr at 25°C. What is the mole fraction of NaCl in this solution? What would be the vapor pressure of this solution at 45°C? The vapor pressure of pure water is 23.8 torr at 25°C and 71.9 torr at 45°C.
49. Pentane (C₅H₁₂) and hexane (C₆H₁₄) form an ideal solution. At 25°C the vapor pressures of pentane and hexane are 511 and 150. torr, respectively. A solution is prepared by mixing 25 mL pentane (density, 0.63 g/mL) with 45 mL hexane (density, 0.66 g/mL).
- What is the vapor pressure of the resulting solution?
 - What is the composition by mole fraction of pentane in the vapor that is in equilibrium with this solution?
50. A solution is prepared by mixing 0.0300 mol CH₂Cl₂ and 0.0500 mol CH₂Br₂ at 25°C. Assuming the solution is ideal, calculate the composition of the vapor (in terms of mole fractions) at 25°C. At 25°C, the vapor pressures of pure CH₂Cl₂ and pure CH₂Br₂ are 133 and 11.4 torr, respectively.
51. What is the composition of a methanol (CH₃OH)–propanol (CH₃CH₂CH₂OH) solution that has a vapor pressure of 174 torr at 40°C? At 40°C, the vapor pressures of pure methanol and pure propanol are 303 and 44.6 torr, respectively. Assume the solution is ideal.
52. Benzene and toluene form an ideal solution. Consider a solution of benzene and toluene prepared at 25°C. Assuming the mole fractions of benzene and toluene in the vapor phase are equal, calculate the composition of the solution. At 25°C the vapor pressures of benzene and toluene are 95 and 28 torr, respectively.
53. Which of the following will have the lowest total vapor pressure at 25°C?
- pure water (vapor pressure = 23.8 torr at 25°C)
 - a solution of glucose in water with $\chi_{\text{C}_6\text{H}_{12}\text{O}_6} = 0.01$
 - a solution of sodium chloride in water with $\chi_{\text{NaCl}} = 0.01$
 - a solution of methanol in water with $\chi_{\text{CH}_3\text{OH}} = 0.2$ (Consider the vapor pressure of both methanol [143 torr at 25°C] and water.)
54. Which of the choices in Exercise 53 has the highest vapor pressure?

55. A solution is made by mixing 50.0 g acetone (CH_3COCH_3) and 50.0 g methanol (CH_3OH). What is the vapor pressure of this solution at 25°C ? What is the composition of the vapor expressed as a mole fraction? Assume ideal solution and gas behavior. (At 25°C the vapor pressures of pure acetone and pure methanol are 271 and 143 torr, respectively.) The actual vapor pressure of this solution is 161 torr. Explain any discrepancies.
56. The vapor pressures of several solutions of water–propanol ($\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$) were determined at various compositions, with the following data collected at 45°C :

$\chi_{\text{H}_2\text{O}}$	Vapor pressure (torr)
0	74.0
0.15	77.3
0.37	80.2
0.54	81.6
0.69	80.6
0.83	78.2
1.00	71.9

- Are solutions of water and propanol ideal? Explain.
- Predict the sign of ΔH_{soln} for water–propanol solutions.
- Are the interactive forces between propanol and water molecules weaker than, stronger than, or equal to the interactive forces between the pure substances? Explain.
- Which of the solutions in the data would have the lowest normal boiling point?

Colligative Properties

57. A solution is prepared by dissolving 4.9 g sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) in 175 g water. Calculate the boiling point of this solution. Sucrose is a nonelectrolyte.
58. A 2.00-g sample of a large biomolecule was dissolved in 15.0 g of carbon tetrachloride. The boiling point of this solution was determined to be 77.85°C . Calculate the molar mass of the biomolecule. For carbon tetrachloride, the boiling-point constant is $5.03^\circ\text{C} \cdot \text{kg/mol}$, and the boiling point of pure carbon tetrachloride is 76.50°C .
59. What mass of glycerin ($\text{C}_3\text{H}_8\text{O}_3$), a nonelectrolyte, must be dissolved in 200.0 g water to give a solution with a freezing point of -1.50°C ?
60. The freezing point of *t*-butanol is 25.50°C and K_f is $9.1^\circ\text{C} \cdot \text{kg/mol}$. Usually *t*-butanol absorbs water on exposure to air. If the freezing point of a 10.0-g sample of *t*-butanol is 24.59°C , how many grams of water are present in the sample?
61. Calculate the freezing point and boiling point of an antifreeze solution that is 50.0% by mass of ethylene glycol ($\text{HOCH}_2\text{CH}_2\text{OH}$) in water. Ethylene glycol is a nonelectrolyte.
62. What volume of ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$), a nonelectrolyte,

must be added to 15.0 L of water to produce an antifreeze solution with a freezing point of -30.0°C ? What is the boiling point of this solution? (The density of ethylene glycol is 1.11 g/cm^3 , and the density of water is 1.00 g/cm^3 .)

63. A 0.350-g sample of a large biomolecule was dissolved in 15.0 g of chloroform, and the freezing-point depression was determined to be 0.240°C . Calculate the molar mass of the biomolecule (K_f for chloroform is $4.70^\circ\text{C} \cdot \text{kg/mol}$).
64. Anthraquinone contains only carbon, hydrogen, and oxygen and has an empirical formula of $\text{C}_7\text{H}_4\text{O}$. The freezing point of camphor is lowered by 22.3°C when 1.32 g anthraquinone is dissolved in 11.4 g camphor. Determine the molecular formula of anthraquinone.
65. a. Calculate the freezing-point depression and osmotic pressure at 25°C of an aqueous solution containing 1.0 g/L of a protein (molar mass = $9.0 \times 10^4 \text{ g/mol}$) if the density of the solution is 1.0 g/cm^3 .
b. Considering your answer to part a, which colligative property, freezing-point depression or osmotic pressure, would be better used to determine the molar masses of large molecules? Explain.
66. An aqueous solution of 10.00 g of catalase, an enzyme found in the liver, has a volume of 1.00 L at 27°C . The solution's osmotic pressure at 27°C is found to be 0.745 torr. Calculate the molar mass of catalase.
67. If the human eye has an osmotic pressure of 8.00 atm at 25°C , what concentration of solute particles in water will provide an isotonic eyedrop solution (a solution with equal osmotic pressure)?
68. How would you prepare 1.0 L of an aqueous solution of sodium chloride having an osmotic pressure of 15 atm at 22°C ?

Properties of Electrolyte Solutions

69. Consider the following solutions:
 $0.010 \text{ } m \text{ Na}_3\text{PO}_4$ in water
 $0.020 \text{ } m \text{ CaBr}_2$ in water
 $0.020 \text{ } m \text{ KCl}$ in water
 $0.020 \text{ } m \text{ HF}$ in water (HF is a weak acid.)
 a. Assuming complete dissociation of the soluble salts, which solution(s) would have the same boiling point as $0.040 \text{ } m \text{ C}_6\text{H}_{12}\text{O}_6$ in water? $\text{C}_6\text{H}_{12}\text{O}_6$ is a nonelectrolyte.
 b. Which solution would have the highest vapor pressure at 28°C ?
 c. Which solution would have the largest freezing-point depression?
70. From the following:
 pure water
 solution of $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ($m = 0.01$) in water
 solution of NaCl ($m = 0.01$) in water
 solution of CaCl_2 ($m = 0.01$) in water

choose the one with the

- a. highest freezing point.
- b. lowest freezing point.
- c. highest boiling point.
- d. lowest boiling point.
- e. highest osmotic pressure.

71. Calculate the freezing point and the boiling point of each of the following aqueous solutions. (Assume complete dissociation.)

- a. 0.050 *m* MgCl₂
- b. 0.050 *m* FeCl₃

72. A water desalination plant is set up near a salt marsh containing water that is 0.10 *M* NaCl. Calculate the minimum pressure that must be applied at 20.°C to purify the water by reverse osmosis. Assume NaCl is completely dissociated.

73. Use the following data for three aqueous solutions of CaCl₂ to calculate the apparent value of the van't Hoff factor.

Molality	Freezing-Point Depression (°C)
0.0225	0.110
0.0910	0.440
0.278	1.330

74. Calculate the freezing point and the boiling point of each of the following solutions using the observed van't Hoff factors in Table 11.6.

- a. 0.050 *m* MgCl₂
- b. 0.050 *m* FeCl₃

75. Calculate the osmotic pressure at 25°C of a 0.50 *M* solution of Ca(NO₃)₂ in water. (Assume that *i* = 3.0.) Would you expect the measured osmotic pressure of 0.50 *M* Ca(NO₃)₂ to be higher or lower than the value you calculated? Explain.

76. In the winter of 1994, record low temperatures were registered throughout the United States. For example, in Champaign, Illinois, a record low of -29°F was registered. At this temperature can salting icy roads with CaCl₂ be effective in melting the ice?

- a. Assume *i* = 3.00 for CaCl₂.
- b. Assume the average value of *i* from Exercise 73. (The solubility of CaCl₂ in cold water is 74.5 g per 100.0 g of water.)

b. If the enthalpy of hydration for NH₄NO₃ is -630. kJ/mol, calculate the lattice energy of NH₄NO₃.

78. In flushing and cleaning columns used in liquid chromatography to remove adsorbed contaminants, a series of solvents is used. Hexane (C₆H₁₄), chloroform (CHCl₃), methanol (CH₃OH), and water are passed through the column in that order. Rationalize the order in terms of intermolecular forces and the mutual solubility (miscibility) of the solvents.

79. Explain the following on the basis of the behavior of atoms and/or ions.

- a. Cooking with water is faster in a pressure cooker than in an open pan.
- b. Salt is used on icy roads.
- c. Melted sea ice from the Arctic Ocean produces fresh water.
- d. CO₂(s) (dry ice) does not have normal boiling point under normal atmospheric conditions, even though CO₂ is a liquid in fire extinguishers.
- e. Adding a solute to a solvent extends the liquid phase over a larger temperature range.

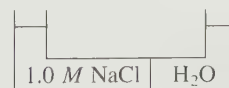
80. Is Henry's law valid for the solubility of CO₂ in a 0.1 *M* NaOH solution? (Hint: CO₂ + OH⁻ → HCO₃⁻.)

81. At 25°C, the vapor in equilibrium with a solution containing carbon disulfide and acetonitrile has a total pressure of 263 torr and is 85.5 mole percent carbon disulfide. What is the mole fraction of carbon disulfide in the solution? At 25°C, the vapor pressure of carbon disulfide is 375 torr. Assume the solution and vapor exhibit ideal behavior.

82. If the fluid inside a tree is about 0.1 *M* more concentrated in solute than the groundwater that bathes the roots, how high will a column of fluid rise in the tree at 25°C? Assume that the density of the fluid is 1.0 g/cm³. (The density of mercury is 13.6 g/cm³.)

83. An unknown compound contains only carbon, hydrogen, and oxygen. Combustion analysis of the compound gives mass percents of 31.57% C and 5.30% H. The molar mass is determined by measuring the freezing-point depression of an aqueous solution. A freezing point of -5.20°C is recorded for a solution made by dissolving 10.56 g of the compound in 25.0 g water. Determine the empirical formula, molar mass, and molecular formula of the compound. Assume that the compound is a nonelectrolyte.

84. Consider the following:



What would happen to the level of liquid in the two arms if the semipermeable membrane separating the two liquids were permeable to

- a. H₂O only?
- b. H₂O, Na⁺, and Cl⁻?

Additional Exercises

77. In a coffee-cup calorimeter, 1.60 g of NH₄NO₃ was mixed with 75.0 g of water at an initial temperature of 25.00°C. After dissolution of the salt, the final temperature of the calorimeter contents was 23.34°C.

- a. Assuming the solution has a heat capacity of 4.18 J/g · °C, and assuming no heat loss to the calorimeter, calculate the enthalpy of solution (Δ*H*_{soln}) for the dissolution of NH₄NO₃ in units of kJ/mol.

85. Consider an aqueous solution containing sodium chloride that has a density of 1.01 g/mL. Assume the solution behaves ideally. The freezing point of this solution at 1.0 atm is -1.28°C . Calculate the percent composition of this solution (by mass).

Challenge Problems

86. An aqueous solution is 1.00% NaCl by mass and has a density of 1.071 g/cm³ at 25°C. The observed osmotic pressure of this solution is 7.83 atm at 25°C.
- What fraction of the moles of NaCl in this solution exist as ion pairs?
 - Calculate the freezing point that would be observed for this solution.
87. The vapor in equilibrium with a pentane–hexane solution at 25°C has a mole fraction of pentane equal to 0.15 at 25°C. What is the mole fraction of pentane in the solution? (See Exercise 49 for the vapor pressures of the pure liquids.)
88. A forensic chemist is given a white solid that is suspected of being pure cocaine ($\text{C}_{17}\text{H}_{21}\text{NO}_4$, molar mass = 303.35 g/mol). She dissolves 1.22 ± 0.01 g of the solid in 15.60 ± 0.01 g benzene. The freezing point is lowered by $1.32 \pm 0.04^{\circ}\text{C}$.
- What is the molar mass of the substance? Assuming that the percent uncertainty in the calculated molar mass is the same as the percent uncertainty in the temperature change, calculate the uncertainty in the molar mass.
 - Could the chemist unequivocally state that the substance is cocaine? For example, is the uncertainty small enough to distinguish cocaine from codeine ($\text{C}_{18}\text{H}_{21}\text{NO}_3$, molar mass = 299.36 g/mol)?
 - Assuming that the absolute uncertainties in the measurements of temperature and mass remain unchanged, how could the chemist improve the precision of her results?
89. A 1.60-g sample of a mixture of naphthalene (C_{10}H_8) and anthracene ($\text{C}_{14}\text{H}_{10}$) is dissolved in 20.0 g benzene (C_6H_6). The freezing point of the solution is 2.81°C . What is the composition as mass percent of the sample mixture? The freezing point of benzene is 5.51°C , and K_f is $5.12^{\circ}\text{C} \cdot \text{kg/mol}$.
90. A solid mixture contains MgCl_2 and NaCl. When 0.5000 g of this solid is dissolved in enough water to form 1.000 L of solution, the osmotic pressure at 25.0°C is observed to be 0.3950 atm. What is the mass percent of MgCl_2 in the solid? (Assume ideal behavior for the solution.)
91. Formic acid (HCO_2H) is a monoprotic acid that ionizes only partially in aqueous solutions. A 0.10 M formic acid solution is 4.2% ionized. Assuming that the molarity and molality of the solution are the same, calculate the freezing point and the boiling point of 0.10 M formic acid.
92. Specifications for lactated Ringer's solution, which is used for intravenous (IV) injections, are as follows to reach 100. mL of solution:

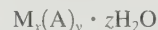
4.9–6.0 mg Ca^{2+}
 368–408 mg Cl^{-}
 231–261 mg lactate, $\text{C}_3\text{H}_5\text{O}_3^{-}$

- Specify the amounts of NaCl, KCl, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, and $\text{NaC}_3\text{H}_5\text{O}_3$ needed to prepare 100. mL of lactated Ringer's solution.
 - What is the range of the osmotic pressure of the solution at 37°C , given the above specifications?
93. In some regions of the southwest United States, the water is very hard. For example, in Las Cruces, New Mexico, the tap water contains about 560 μg of dissolved solids per milliliter. Reverse osmosis units are marketed in this area to soften water. A typical unit exerts a pressure of 8.0 atm and can produce 45 L of water per day.
- Assuming all of the dissolved solids are MgCO_3 and assuming a temperature of 27°C , what total volume of water must be processed to produce 45 L of pure water?
 - Would the same system work for purifying seawater? (Assume seawater is 0.60 M NaCl.)

Marathon Problem*

This problem is designed to incorporate several concepts and techniques into one situation. Marathon Problems can be used in class by groups of students to help facilitate problem-solving skills.

94. Using the following information, identify the strong electrolyte whose general formula is



Ignore the effect of interionic attractions in the solution.

- A^{n-} is a common oxyanion. When 30.0 mg of the anhydrous sodium salt containing this oxyanion (Na_nA , where $n = 1, 2, \text{ or } 3$) is reduced, 15.26 mL of 0.02313 M reducing agent is required to react completely with the Na_nA present. Assume a 1:1 mole ratio in the reaction.
- The cation is derived from a silvery white metal that is relatively expensive. The metal itself crystallizes in a body-centered cubic unit cell and has an atomic radius of 198.4 pm. The solid, pure metal has a density of 5.243 g/cm^3 . The oxidation number of M in the strong electrolyte in question is +3.
- When 33.45 mg of the compound is present (dissolved) in 10.0 mL of aqueous solution at 25°C , the solution has an osmotic pressure of 558 torr.

* This Marathon Problem was developed by James H. Burness, Penn State University, York Campus. Reprinted with permission from the *Journal of Chemical Education*, Vol. 68, No. 11, 1991, pp. 919–922; copyright © 1991, Division of Chemical Education, Inc.

285–315 mg Na^{+}
 14.1–17.3 mg K^{+}

 Media Activities

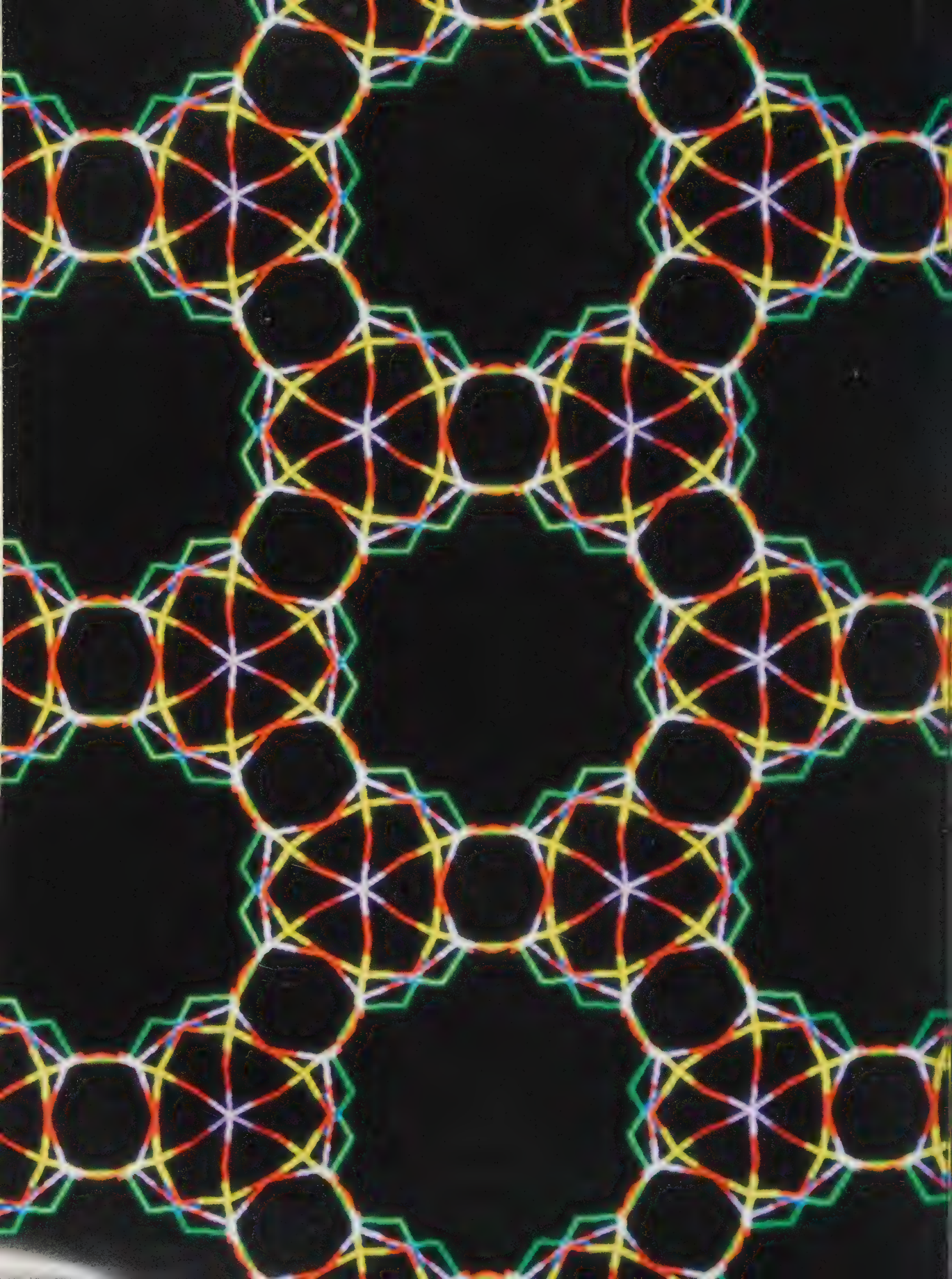
1. Open the Dissolution of a Solid in a Liquid Visualization on the student CD to review the hydration process for an ionic compound. To calculate the heat of a solution (ΔH_{soln}) when an ionic compound dissolves in water, you need to know the lattice energy of the ionic compound and the enthalpy change when the gaseous ions are hydrated (called the heat of hydration, ΔH_{hyd}).
 - a. Using NaCl as an example, write out the chemical equation where ΔH equals the lattice energy. Write out the equation for ΔH_{hyd} and ΔH_{soln} .

- b. Using Hess's law, show how to manipulate the lattice energy equation and the ΔH_{hyd} equation to come up with the ΔH_{soln} equation. If ΔH_{soln} for NaCl is 3 kJ/mol and the lattice energy for NaCl is -786 kJ/mol, determine ΔH_{hyd} for NaCl. For more practice with this type of problem, do Exercises 11.33–11.36 in the text. Do Exercise 11.77 to review calorimetry problems.

2. Test your understanding of Chapter 11 material by taking the ACE quizzes on the student web site.

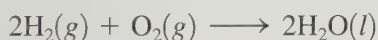


For additional web activities and other resources, visit the Zumdahl, *Chemistry*, Sixth Edition textbook site at <http://chemistry.college.hmco.com/students>.

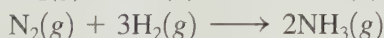
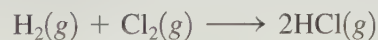


Chemical Kinetics

The applications of chemistry focus largely on chemical reactions, and the commercial use of a reaction requires knowledge of several of its characteristics, including its stoichiometry, energetics, and rate. A reaction is defined by its reactants and products, whose identity must be learned by experiment. Once the reactants and products are known, the equation for the reaction can be written and balanced, and stoichiometric calculations can be carried out. Another very important characteristic of a reaction is its spontaneity. Spontaneity refers to the *inherent tendency* for the process to occur; however, it implies nothing about speed. *Spontaneous does not mean fast*. There are many spontaneous reactions that are so slow that no apparent reaction occurs over a period of weeks or years at normal temperatures. For example, there is a strong inherent tendency for gaseous hydrogen and oxygen to combine, that is,



but in fact the two gases can coexist indefinitely at 25°C. Similarly, the gaseous reactions



are both highly likely to occur from a thermodynamic standpoint, but we observe no reactions under normal conditions. In addition, the process of changing diamond to graphite is spontaneous but is so slow that it is not detectable.

To be useful, reactions must occur at a reasonable rate. To produce the 20 million tons of ammonia needed each year for fertilizer, we cannot simply mix nitrogen and hydrogen gases at 25°C and wait for them to react. It

A computer simulation of a porous aluminophosphate sheet, a potential solid-state catalyst. The atoms are indicated by colors: aluminum (yellow), phosphorus (light purple), oxygen (red), carbon (green), and nitrogen (blue).

CONTENTS

12.1 Reaction Rates

12.2 Rate Laws: An Introduction

- Types of Rate Laws

12.3 Determining the Form of the Rate Law

- Method of Initial Rates

12.4 The Integrated Rate Law

- First-Order Rate Laws
- Half-Life of a First-Order Reaction
- Second-Order Rate Laws
- Zero-Order Rate Laws
- Integrated Rate Laws for Reactions with More Than One Reactant

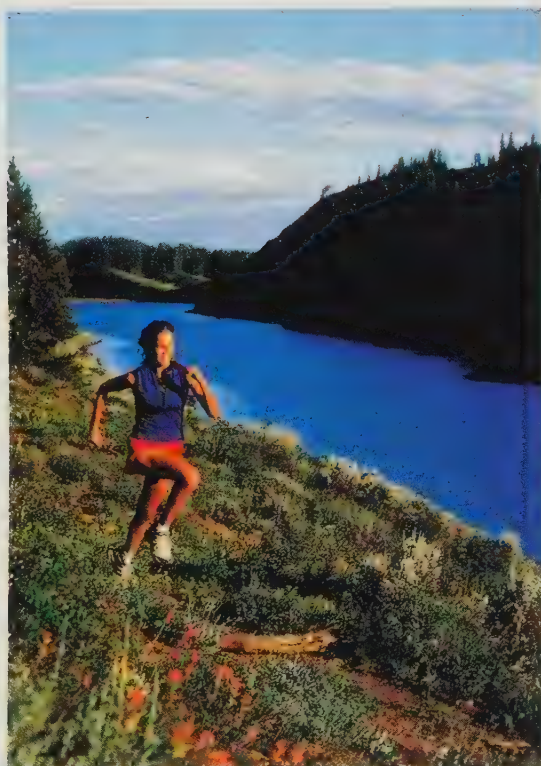
12.5 Rate Laws: A Summary

12.6 Reaction Mechanisms

12.7 A Model for Chemical Kinetics

12.8 Catalysis

- Heterogeneous Catalysis
- Homogeneous Catalysis



The energy required for athletic exertion, the breaching of an Orca whale, and the combustion of fuel in a race car all result from chemical reactions.

is not enough to understand the stoichiometry and thermodynamics of a reaction; we also must understand the factors that govern the rate of the reaction. The area of chemistry that concerns reaction rates is called **chemical kinetics**.

One of the main goals of chemical kinetics is to understand the steps by which a reaction takes place. This series of steps is called the *reaction mechanism*. Understanding the mechanism allows us to find ways to facilitate the reaction. For example, the Haber process for the production of ammonia requires high temperatures to achieve commercially feasible reaction rates. However, even higher temperatures (and more cost) would be required without the use of iron oxide, which speeds up the reaction.

In this chapter we will consider the main ideas of chemical kinetics. We will explore rate laws, reaction mechanisms, and simple models for chemical reactions.

12.1 Reaction Rates

The kinetics of air pollution is discussed in Section 12.8.

To introduce the concept of the rate of a reaction, we will consider the decomposition of nitrogen dioxide, a gas that causes air pollution. Nitrogen dioxide decomposes to nitric oxide and oxygen as follows:



Suppose in a particular experiment we start with a flask of nitrogen dioxide at 300°C and measure the concentrations of nitrogen dioxide, nitric oxide, and oxygen as the nitrogen dioxide decomposes. The results of this experiment are summarized in Table 12.1, and the data are plotted in Fig. 12.1.

Note from these results that the concentration of the reactant (NO_2) decreases with time and the concentrations of the products (NO and O_2) increase with time (see Fig. 12.2). Chemical kinetics deals with the speed at which these changes occur. The speed, or *rate*, of a process is defined as the change in a given quantity over a specific period of time. For chemical reactions, the quantity that changes is the amount or concentration of a reactant or product. So the **reaction rate** of a chemical reaction is defined as the *change in concentration of a reactant or product per unit time*:

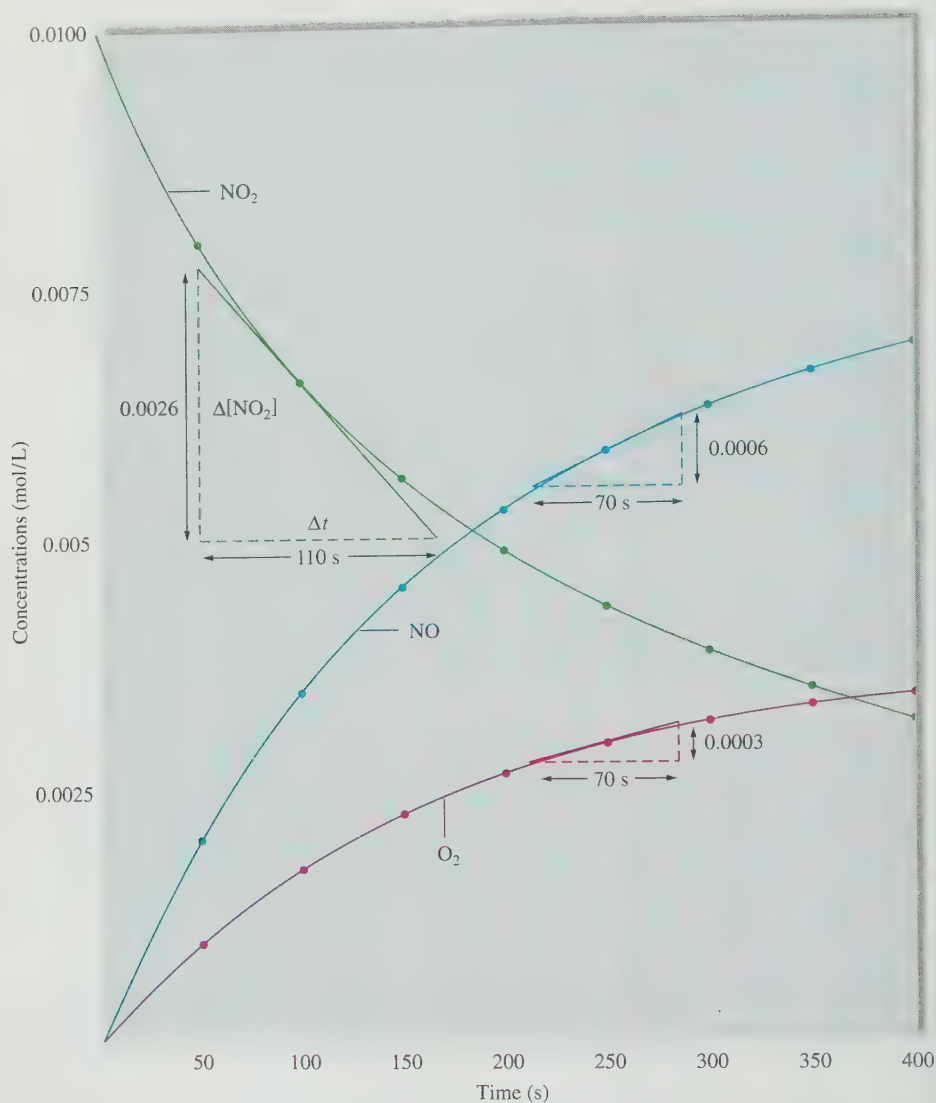
$$\begin{aligned} \text{Rate} &= \frac{\text{concentration of A at time } t_2 - \text{concentration of A at time } t_1}{t_2 - t_1} \\ &= \frac{\Delta[\text{A}]}{\Delta t} \end{aligned}$$

[A] means concentration of A in mol/L.

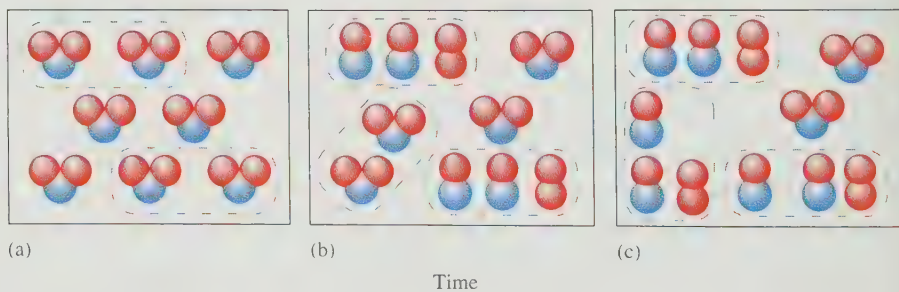
where A is the reactant or product being considered, and the square brackets indicate concentration in mol/L. As usual, the symbol Δ indicates a *change* in a given quantity. Note that a change can be positive (increase) or negative (decrease), thus leading to a positive or negative reaction rate by this definition. However, for convenience, we will always define the rate as a positive quantity, as we will see.

TABLE 12.1 Concentrations of Reactant and Products as a Function of Time for the Reaction $2\text{NO}_2(g) \rightarrow 2\text{NO}(g) + \text{O}_2(g)$ (at 300°C)

Time (± 1 s)	Concentration (mol/L)		
	NO_2	NO	O_2
0	0.0100	0	0
50	0.0079	0.0021	0.0011
100	0.0065	0.0035	0.0018
150	0.0055	0.0045	0.0023
200	0.0048	0.0052	0.0026
250	0.0043	0.0057	0.0029
300	0.0038	0.0062	0.0031
350	0.0034	0.0066	0.0033
400	0.0031	0.0069	0.0035

**FIGURE 12.1**

Starting with a flask of nitrogen dioxide at 300°C , the concentrations of nitrogen dioxide, nitric oxide, and oxygen are plotted versus time.

**FIGURE 12.2**

Representation of the reaction $2\text{NO}_2(\text{g}) \rightarrow 2\text{NO}(\text{g}) + \text{O}_2(\text{g})$. (a) The reaction at the very beginning ($t = 0$). (b) and (c) As time passes, NO_2 is converted to NO and O_2 .

Now let us calculate the average rate at which the concentration of NO_2 changes over the first 50 seconds of the reaction using the data given in Table 12.1.

$$\begin{aligned}\frac{\text{Change in } [\text{NO}_2]}{\text{Time elapsed}} &= \frac{\Delta[\text{NO}_2]}{\Delta t} \\ &= \frac{[\text{NO}_2]_{t=50} - [\text{NO}_2]_{t=0}}{50. \text{ s} - 0 \text{ s}} \\ &= \frac{0.0079 \text{ mol/L} - 0.0100 \text{ mol/L}}{50. \text{ s}} \\ &= -4.2 \times 10^{-5} \text{ mol/L} \cdot \text{s}\end{aligned}$$

Note that since the concentration of NO_2 decreases with time, $\Delta[\text{NO}_2]$ is a negative quantity. Because it is customary to work with *positive* reaction rates, we define the rate of this particular reaction as

$$\text{Rate} = -\frac{\Delta[\text{NO}_2]}{\Delta t}$$

Since the concentrations of reactants always decrease with time, any rate expression involving a reactant will include a negative sign. The average rate of this reaction from 0 to 50 seconds is then

$$\begin{aligned}\text{Rate} &= -\frac{\Delta[\text{NO}_2]}{\Delta t} \\ &= -(-4.2 \times 10^{-5} \text{ mol/L} \cdot \text{s}) \\ &= 4.2 \times 10^{-5} \text{ mol/L} \cdot \text{s}\end{aligned}$$

The average rates for this reaction during several other time intervals are given in Table 12.2. *Note that the rate is not constant but decreases with time.* The rates given in Table 12.2 are *average rates* over 50-second time intervals. The value of the rate at a particular time (the **instantaneous rate**) can be obtained by computing the slope of a line tangent to the curve at that point. Figure 12.1 shows a tangent drawn at $t = 100$ seconds. The *slope* of this line gives the rate at $t = 100$ seconds as follows:

$$\begin{aligned}\text{Slope of the tangent line} &= \frac{\text{change in } y}{\text{change in } x} \\ &= \frac{\Delta[\text{NO}_2]}{\Delta t}\end{aligned}$$

But

$$\text{Rate} = -\frac{\Delta[\text{NO}_2]}{\Delta t}$$

Therefore,

$$\begin{aligned}\text{Rate} &= -(\text{slope of the tangent line}) \\ &= -\left(\frac{-0.0026 \text{ mol/L}}{110 \text{ s}}\right) \\ &= 2.4 \times 10^{-5} \text{ mol/L} \cdot \text{s}\end{aligned}$$

So far we have discussed the rate of this reaction only in terms of the reactant. The rate also can be defined in terms of the products. However, in doing so we must take into account the coefficients in the balanced equation for the reaction, because

Appendix 1.3 reviews slopes of straight lines.

TABLE 12.2
Average Rate (in $\text{mol/L} \cdot \text{s}$) of
Decomposition of Nitrogen
Dioxide as a Function of
Time*

$-\frac{\Delta[\text{NO}_2]}{\Delta t}$	Time Period (s)
4.2×10^{-5}	0 $\rightarrow$ 50
2.8×10^{-5}	50 $\rightarrow$ 100
2.0×10^{-5}	100 $\rightarrow$ 150
1.4×10^{-5}	150 $\rightarrow$ 200
1.0×10^{-5}	200 $\rightarrow$ 250

*Note that the *rate* decreases with time.



Los Angeles on a clear day, and on a day when air pollution is significant.

the stoichiometry determines the relative rates of consumption of reactants and generation of products. For example, in the reaction we are considering,



both the reactant NO_2 and the product NO have a coefficient of 2, so NO is produced at the same rate as NO_2 is consumed. We can verify this from Fig. 12.1. Note that the curve for NO is the same shape as the curve for NO_2 , except that it is inverted, or flipped over. This means that, at any point in time, the slope of the tangent to the curve for NO will be the negative of the slope to the curve for NO_2 . (Verify this at the point $t = 100$ seconds on both curves.) In the balanced equation, the product O_2 has a coefficient of 1, which means it is produced half as fast as NO , since NO has a coefficient of 2. That is, the rate of NO production is twice the rate of O_2 production.

We also can verify this fact from Fig. 12.1. For example, at $t = 250$ seconds,

$$\begin{aligned} \text{Slope of the tangent to the NO curve} &= \frac{6.0 \times 10^{-4} \text{ mol/L}}{70. \text{ s}} \\ &= 8.6 \times 10^{-6} \text{ mol/L} \cdot \text{s} \\ \text{Slope of the tangent to the O}_2 \text{ curve} &= \frac{3.0 \times 10^{-4} \text{ mol/L}}{70. \text{ s}} \\ &= 4.3 \times 10^{-6} \text{ mol/L} \cdot \text{s} \end{aligned}$$

The slope at $t = 250$ seconds on the NO curve is twice the slope of that point on the O_2 curve, showing that the rate of production of NO is twice that of O_2 .

The rate information can be summarized as follows:

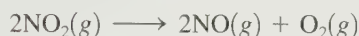
Rate of consumption of NO_2	=	rate of production of NO	=	$2(\text{rate of production of } \text{O}_2)$
$-\frac{\Delta[\text{NO}_2]}{\Delta t}$	=	$\frac{\Delta[\text{NO}]}{\Delta t}$	=	$2\left(\frac{\Delta[\text{O}_2]}{\Delta t}\right)$

We have seen that the rate of a reaction is not constant, but that it changes with time. This is so because the concentrations change with time (Fig. 12.1).

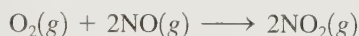
Because the reaction rate changes with time, and because the rate is different (by factors that depend on the coefficients in the balanced equation) depending on which reactant or product is being studied, we must be very specific when we describe a rate for a chemical reaction.

12.2 Rate Laws: An Introduction

Chemical reactions are *reversible*. In our discussion of the decomposition of nitrogen dioxide, we have so far considered only the *forward reaction*, as shown here:



However, the *reverse reaction* also can occur. As NO and O₂ accumulate, they can react to re-form NO₂:



When gaseous NO₂ is placed in an otherwise empty container, initially the dominant reaction is



and the change in the concentration of NO₂ ($\Delta[\text{NO}_2]$) depends only on the forward reaction. However, after a period of time, enough products accumulate so that the reverse reaction becomes important. Now $\Delta[\text{NO}_2]$ depends on the *difference in the rates of the forward and reverse reactions*. This complication can be avoided if we study the rate of a reaction under conditions where the reverse reaction makes only a negligible contribution. Typically, this means that we must study a reaction at a point soon after the reactants are mixed, before the products have had time to build up to significant levels.

If we choose conditions where the reverse reaction can be neglected, the *reaction rate will depend only on the concentrations of the reactants*. For the decomposition of nitrogen dioxide, we can write

$$\text{Rate} = k[\text{NO}_2]^n \quad (12.1)$$

Such an expression, which shows how the rate depends on the concentrations of reactants, is called a **rate law**. The proportionality constant k , called the **rate constant**, and n , called the **order** of the reactant, must both be determined by experiment. The order of a reactant can be an integer (including zero) or a fraction. For the relatively simple reactions we will consider in this book, the orders will often be positive integers.

Note two important points about Equation (12.1):

1. The concentrations of the products do not appear in the rate law because the reaction rate is being studied under conditions where the reverse reaction does not contribute to the overall rate.
2. The value of the exponent n must be determined by experiment; it cannot be written from the balanced equation.

Before we go further we must define exactly what we mean by the term *rate* in Equation (12.1). In Section 12.1 we saw that reaction rate means a change in con-

When forward and reverse reaction rates are equal, there will be no changes in the concentrations of reactants or products. This is called *chemical equilibrium* and is discussed fully in Chapter 13.

centration per unit time. However, which reactant or product concentration do we choose in defining the rate? For example, for the decomposition of NO_2 to produce O_2 and NO considered in Section 12.1, we could define the rate in terms of any of these three species. However, since O_2 is produced only half as fast as NO , we must be careful to specify which species we are talking about in a given case. For instance, we might choose to define the reaction rate in terms of the consumption of NO_2 :

$$\text{Rate} = -\frac{\Delta[\text{NO}_2]}{\Delta t} = k[\text{NO}_2]^n$$

On the other hand, we could define the rate in terms of the production of O_2 :

$$\text{Rate}' = \frac{\Delta[\text{O}_2]}{\Delta t} = k'[\text{NO}_2]^n$$

Note that because 2NO_2 molecules are consumed for every O_2 molecule produced,

$$\text{Rate} = 2 \times \text{rate}'$$

or

$$k[\text{NO}_2]^n = 2k'[\text{NO}_2]^n$$

and

$$k = 2 \times k'$$

Thus the value of the rate constant depends on how the rate is defined.

In this text we will always be careful to define exactly what is meant by the rate for a given reaction so that there will be no confusion about which specific rate constant is being used.

Types of Rate Laws

Notice that the rate law we have used to this point expresses rate as a function of concentration. For example, for the decomposition of NO_2 we have defined

$$\text{Rate} = -\frac{\Delta[\text{NO}_2]}{\Delta t} = k[\text{NO}_2]^n$$

which tells us (once we have determined the value of n) exactly how the rate depends on the concentration of the reactant, NO_2 . A rate law that expresses how the *rate depends on concentration* is technically called the **differential rate law**, but it is often simply called the **rate law**. Thus when we use the term *the rate law* in this text, we mean the expression that gives the rate as a function of concentration.

A second kind of rate law, the **integrated rate law**, also will be important in our study of kinetics. The integrated rate law expresses how the *concentrations depend on time*. Although we will not consider the details here, a given differential rate law is always related to a certain type of integrated rate law, and vice versa. That is, if we determine the differential rate law for a given reaction, we automatically know the form of the integrated rate law for the reaction. This means that once we determine experimentally either type of rate law for a reaction, we also know the other one.

Which rate law we choose to determine by experiment often depends on what types of data are easiest to collect. If we can conveniently measure how the rate changes as the concentrations are changed, we can readily determine the differential (rate/concentration) rate law. On the other hand, if it is more convenient to meas-

The name *differential rate law* comes from a mathematical term. We will regard it simply as a label. The terms *differential rate law* and *rate law* will be used interchangeably in this text.

ure the concentration as a function of time, we can determine the form of the integrated (concentration/time) rate law. We will discuss how rate laws are actually determined in the next several sections.

Why are we interested in determining the rate law for a reaction? How does it help us? It helps us because we can work backward from the rate law to infer the steps by which the reaction occurs. Most chemical reactions do not take place in a single step but result from a series of sequential steps. To understand a chemical reaction, we must learn what these steps are. For example, a chemist who is designing an insecticide may study the reactions involved in the process of insect growth to see what type of molecule might interrupt this series of reactions. Or an industrial chemist may be trying to make a given reaction occur faster. To accomplish this, he or she must know which step is slowest, because it is that step that must be speeded up. Thus a chemist is usually not interested in a rate law for its own sake but because of what it reveals about the steps by which a reaction occurs. We will develop a process for finding the reaction steps in this chapter.

Rate Laws: A Summary

■ There are two types of rate laws.

1. The *differential rate law* (often called simply the *rate law*) shows how the rate of a reaction depends on concentrations.
2. The *integrated rate law* shows how the concentrations of species in the reaction depend on time.

■ Because we typically consider reactions only under conditions where the reverse reaction is unimportant, our rate laws will involve only concentrations of reactants.

■ Because the differential and integrated rate laws for a given reaction are related in a well-defined way, the experimental determination of *either* of the rate laws is sufficient.

■ Experimental convenience usually dictates which type of rate law is determined experimentally.

■ Knowing the rate law for a reaction is important mainly because we can usually infer the individual steps involved in the reaction from the specific form of the rate law.

12.3 Determining the Form of the Rate Law

The first step in understanding how a given chemical reaction occurs is to determine the *form* of the rate law. That is, we need to determine experimentally the power to which each reactant concentration must be raised in the rate law. In this section we will explore ways to obtain the differential rate law for a reaction. First, we will consider the decomposition of dinitrogen pentoxide in carbon tetrachloride solution:

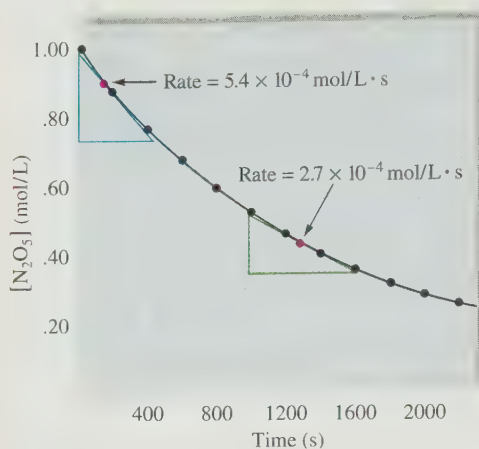


Data for this reaction at 45°C are listed in Table 12.3 and plotted in Fig. 12.3. In this reaction the oxygen gas escapes from the solution and thus does not react with the nitrogen dioxide, so we do not have to be concerned about the effects of the reverse reaction at any time over the life of the reaction. That is, the reverse reaction is negligible at all times over the course of this reaction.

TABLE 12.3

Concentration/Time Data for the Reaction $2\text{N}_2\text{O}_5(\text{soln}) \rightarrow 4\text{NO}_2(\text{soln}) + \text{O}_2(\text{g})$ (at 45°C)

$[\text{N}_2\text{O}_5]$ (mol/L)	Time (s)
1.00	0
0.88	200
0.78	400
0.69	600
0.61	800
0.54	1000
0.48	1200
0.43	1400
0.38	1600
0.34	1800
0.30	2000

**FIGURE 12.3**

A plot of the concentration of N_2O_5 as a function of time for the reaction $2\text{N}_2\text{O}_5(\text{soln}) \rightarrow 4\text{NO}_2(\text{soln}) + \text{O}_2(\text{g})$ (at 45°C). Note that the reaction rate at $[\text{N}_2\text{O}_5] = 0.90\text{ M}$ is twice that at $[\text{N}_2\text{O}_5] = 0.45\text{ M}$.

Evaluation of the reaction rates at concentrations of N_2O_5 of 0.90 M and 0.45 M , by taking the slopes of the tangents to the curve at these points (see Fig. 12.3), yields the following data:

$[\text{N}_2\text{O}_5]$	Rate (mol/L · s)
0.90 M	5.4×10^{-4}
0.45 M	2.7×10^{-4}

Note that when $[\text{N}_2\text{O}_5]$ is halved, the rate is also halved. This means that the rate of this reaction depends on the concentration of N_2O_5 to the *first power*. In other words, the (differential) rate law for this reaction is

$$\text{Rate} = -\frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} = k[\text{N}_2\text{O}_5]^1 = k[\text{N}_2\text{O}_5]$$

First order: rate = $k[A]$. Doubling the concentration of A doubles the reaction rate.

Thus the reaction is *first order* in N_2O_5 . Note that for this reaction the order is *not* the same as the coefficient of N_2O_5 in the balanced equation for the reaction. This reemphasizes the fact that the order of a particular reactant must be obtained by *observing* how the reaction rate depends on the concentration of that reactant.

We have seen that by determining the instantaneous rate at two different reactant concentrations, the rate law for the decomposition of N_2O_5 is shown to have the form

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]$$

where A represents N_2O_5 .

Method of Initial Rates

The value of the initial rate is determined for each experiment at the same value of t as close to $t = 0$ as possible.

One common method for experimentally determining the form of the rate law for a reaction is the **method of initial rates**. The **initial rate** of a reaction is the instantaneous rate determined just after the reaction begins (just after $t = 0$). The idea is

TABLE 12.4 Initial Rates from Three Experiments for the Reaction $\text{NH}_4^+(\text{aq}) + \text{NO}_2^-(\text{aq}) \rightarrow \text{N}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$

Experiment	Initial Concentration of NH_4^+	Initial Concentration of NO_2^-	Initial Rate ($\text{mol/L} \cdot \text{s}$)
1	0.100 M	0.0050 M	1.35×10^{-7}
2	0.100 M	0.010 M	2.70×10^{-7}
3	0.200 M	0.010 M	5.40×10^{-7}



Visualization: Reaction Rate and Concentration

to determine the instantaneous rate before the initial concentrations of reactants have changed significantly. Several experiments are carried out using different initial concentrations, and the initial rate is determined for each run. The results are then compared to see how the initial rate depends on the initial concentrations. This allows the form of the rate law to be determined. We will illustrate the method of initial rates using the following equation:

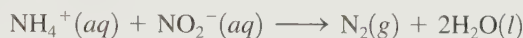


Table 12.4 gives initial rates obtained from three experiments involving different initial concentrations of reactants. The general form of the rate law for this reaction is

$$\text{Rate} = -\frac{\Delta[\text{NH}_4^+]}{\Delta t} = k[\text{NH}_4^+]^n[\text{NO}_2^-]^m$$

We can determine the values of n and m by observing how the initial rate depends on the initial concentrations of NH_4^+ and NO_2^- . In Experiments 1 and 2, where the initial concentration of NH_4^+ remains the same but the initial concentration of NO_2^- doubles, the observed initial rate also doubles. Since

$$\text{Rate} = k[\text{NH}_4^+]^n[\text{NO}_2^-]^m$$

we have for Experiment 1

$$\text{Rate} = 1.35 \times 10^{-7} \text{ mol/L} \cdot \text{s} = k(0.100 \text{ mol/L})^n(0.0050 \text{ mol/L})^m$$

and for Experiment 2

$$\text{Rate} = 2.70 \times 10^{-7} \text{ mol/L} \cdot \text{s} = k(0.100 \text{ mol/L})^n(0.010 \text{ mol/L})^m$$

The ratio of these rates is

$$\begin{aligned} \frac{\text{Rate 2}}{\text{Rate 1}} &= \frac{2.70 \times 10^{-7} \text{ mol/L} \cdot \text{s}}{1.35 \times 10^{-7} \text{ mol/L} \cdot \text{s}} = \frac{k(0.100 \text{ mol/L})^n(0.010 \text{ mol/L})^m}{k(0.100 \text{ mol/L})^n(0.0050 \text{ mol/L})^m} \\ &= \frac{(0.010 \text{ mol/L})^m}{(0.0050 \text{ mol/L})^m} = (2.0)^m \end{aligned}$$

Rates 1, 2, and 3 were determined at the same value of t (very close to $t = 0$).

Thus

$$\frac{\text{Rate 2}}{\text{Rate 1}} = 2.00 = (2.0)^m$$

which means the value of m is 1. The rate law for this reaction is first order in the reactant NO_2^- .

A similar analysis of the results for Experiments 2 and 3 yields the ratio

$$\begin{aligned}\frac{\text{Rate 3}}{\text{Rate 2}} &= \frac{5.40 \times 10^{-7} \text{ mol/L} \cdot \text{s}}{2.70 \times 10^{-7} \text{ mol/L} \cdot \text{s}} = \frac{(0.200 \text{ mol/L})^n}{(0.100 \text{ mol/L})^n} \\ &= 2.00 = \left(\frac{0.200}{0.100}\right)^n = (2.00)^n\end{aligned}$$

The value of n is also 1.

We have shown that the values of n and m are both 1 and the rate law is

$$\text{Rate} = k[\text{NH}_4^+][\text{NO}_2^-]$$

This rate law is first order in both NO_2^- and NH_4^+ . Note that it is merely a coincidence that n and m have the same values as the coefficients of NH_4^+ and NO_2^- in the balanced equation for the reaction.

Overall reaction order is the sum of the orders for the various reactants.

The **overall reaction order** is the sum of n and m . For this reaction, $n + m = 2$. The reaction is second order overall.

The value of the rate constant k can now be calculated using the results of *any* of the three experiments shown in Table 12.4. From the data for Experiment 1, we know that

$$\begin{aligned}\text{Rate} &= k[\text{NH}_4^+][\text{NO}_2^-] \\ 1.35 \times 10^{-7} \text{ mol/L} \cdot \text{s} &= k(0.100 \text{ mol/L})(0.0050 \text{ mol/L})\end{aligned}$$

Then

$$k = \frac{1.35 \times 10^{-7} \text{ mol/L} \cdot \text{s}}{(0.100 \text{ mol/L})(0.0050 \text{ mol/L})} = 2.7 \times 10^{-4} \text{ L/mol} \cdot \text{s}$$

SAMPLE EXERCISE 12.1

Determining a Rate Law

The reaction between bromate ions and bromide ions in acidic aqueous solution is given by the equation

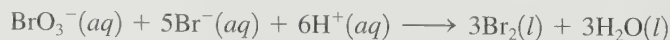


Table 12.5 gives the results from four experiments. Using these data, determine the orders for all three reactants, the overall reaction order, and the value of the rate constant.

TABLE 12.5 The Results from Four Experiments to Study the Reaction $\text{BrO}_3^-(aq) + 5\text{Br}^-(aq) + 6\text{H}^+(aq) \rightarrow 3\text{Br}_2(l) + 3\text{H}_2\text{O}(l)$

Experiment	Initial Concentration of BrO_3^- (mol/L)	Initial Concentration of Br^- (mol/L)	Initial Concentration of H^+ (mol/L)	Measured Initial Rate (mol/L · s)
1	0.10	0.10	0.10	8.0×10^{-4}
2	0.20	0.10	0.10	1.6×10^{-3}
3	0.20	0.20	0.10	3.2×10^{-3}
4	0.10	0.10	0.20	3.2×10^{-3}

SOLUTION

The general form of the rate law for this reaction is

$$\text{Rate} = k[\text{BrO}_3^-]^n[\text{Br}^-]^m[\text{H}^+]^p$$

We can determine the values of n , m , and p by comparing the rates from the various experiments. To determine the value of n , we use the results from Experiments 1 and 2, in which only $[\text{BrO}_3^-]$ changes:

$$\begin{aligned}\frac{\text{Rate 2}}{\text{Rate 1}} &= \frac{1.6 \times 10^{-3} \text{ mol/L} \cdot \text{s}}{8.0 \times 10^{-4} \text{ mol/L} \cdot \text{s}} = \frac{k(0.20 \text{ mol/L})^n(0.10 \text{ mol/L})^m(0.10 \text{ mol/L})^p}{k(0.10 \text{ mol/L})^n(0.10 \text{ mol/L})^m(0.10 \text{ mol/L})^p} \\ 2.0 &= \left(\frac{0.20 \text{ mol/L}}{0.10 \text{ mol/L}}\right)^n = (2.0)^n\end{aligned}$$

Thus n is equal to 1.

To determine the value of m , we use the results from Experiments 2 and 3, in which only $[\text{Br}^-]$ changes:

$$\begin{aligned}\frac{\text{Rate 3}}{\text{Rate 2}} &= \frac{3.2 \times 10^{-3} \text{ mol/L} \cdot \text{s}}{1.6 \times 10^{-3} \text{ mol/L} \cdot \text{s}} = \frac{k(0.20 \text{ mol/L})^n(0.20 \text{ mol/L})^m(0.10 \text{ mol/L})^p}{k(0.20 \text{ mol/L})^n(0.10 \text{ mol/L})^m(0.10 \text{ mol/L})^p} \\ 2.0 &= \left(\frac{0.20 \text{ mol/L}}{0.10 \text{ mol/L}}\right)^m = (2.0)^m\end{aligned}$$

Thus m is equal to 1.

To determine the value of p , we use the results from Experiments 1 and 4, in which $[\text{BrO}_3^-]$ and $[\text{Br}^-]$ are constant but $[\text{H}^+]$ differs:

$$\begin{aligned}\frac{\text{Rate 4}}{\text{Rate 1}} &= \frac{3.2 \times 10^{-3} \text{ mol/L} \cdot \text{s}}{8.0 \times 10^{-4} \text{ mol/L} \cdot \text{s}} = \frac{k(0.10 \text{ mol/L})^n(0.10 \text{ mol/L})^m(0.20 \text{ mol/L})^p}{k(0.10 \text{ mol/L})^n(0.10 \text{ mol/L})^m(0.10 \text{ mol/L})^p} \\ 4.0 &= \left(\frac{0.20 \text{ mol/L}}{0.10 \text{ mol/L}}\right)^p \\ 4.0 &= (2.0)^p = (2.0)^2\end{aligned}$$

Thus p is equal to 2.

The rate of this reaction is first order in BrO_3^- and Br^- and second order in H^+ . The overall reaction order is $n + m + p = 4$.

The rate law can now be written

$$\text{Rate} = k[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2$$

The value of the rate constant k can be calculated from the results of any of the four experiments. For Experiment 1, the initial rate is $8.0 \times 10^{-4} \text{ mol/L} \cdot \text{s}$ and $[\text{BrO}_3^-] = 0.100 \text{ M}$, $[\text{Br}^-] = 0.10 \text{ M}$, and $[\text{H}^+] = 0.10 \text{ M}$. Using these values in the rate law gives

$$\begin{aligned}8.0 \times 10^{-4} \text{ mol/L} \cdot \text{s} &= k(0.10 \text{ mol/L})(0.10 \text{ mol/L})(0.10 \text{ mol/L})^2 \\ 8.0 \times 10^{-4} \text{ mol/L} \cdot \text{s} &= k(1.0 \times 10^{-4} \text{ mol}^4/\text{L}^4) \\ k &= \frac{8.0 \times 10^{-4} \text{ mol/L} \cdot \text{s}}{1.0 \times 10^{-4} \text{ mol}^4/\text{L}^4} = 8.0 \text{ L}^3/\text{mol}^3 \cdot \text{s}\end{aligned}$$

CHECK:

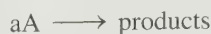
Verify that the same value of k can be obtained from the results of the other experiments.

See Exercises 12.21 through 12.24.

12.4 The Integrated Rate Law

The rate laws we have considered so far express the rate as a function of the reactant concentrations. It is also useful to be able to express the reactant concentrations as a function of time, given the (differential) rate law for the reaction. In this section we show how this is done.

We will proceed by first looking at reactions involving a single reactant:



all of which have a rate law of the form

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]^n$$

We will develop the integrated rate laws individually for the cases $n = 1$ (first order), $n = 2$ (second order), and $n = 0$ (zero order).

First-Order Rate Laws

For the reaction



we have found that the rate law is

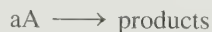
$$\text{Rate} = -\frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} = k[\text{N}_2\text{O}_5]$$

Since the rate of this reaction depends on the concentration of N_2O_5 to the first power, it is a **first-order reaction**. This means that if the concentration of N_2O_5 in a flask were suddenly doubled, the rate of production of NO_2 and O_2 also would double. This rate law can be put into a different form using a calculus operation known as integration, which yields the expression

$$\ln[\text{N}_2\text{O}_5] = -kt + \ln[\text{N}_2\text{O}_5]_0$$

where $\ln$ indicates the natural logarithm, t is the time, $[\text{N}_2\text{O}_5]$ is the concentration of N_2O_5 at time t , and $[\text{N}_2\text{O}_5]_0$ is the initial concentration of N_2O_5 (at $t = 0$, the start of the experiment). Note that such an equation, called the *integrated rate law*, expresses the *concentration of the reactant as a function of time*.

For a chemical reaction of the form



where the kinetics are first order in $[A]$, the rate law is

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]$$

and the **integrated first-order rate law** is

$$\ln[A] = -kt + \ln[A]_0 \quad (12.2)$$

There are several important things to note about Equation (12.2):

Appendix 1.2 contains a review of logarithms.

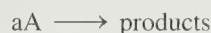
An integrated rate law relates concentration to reaction time.

1. The equation shows how the concentration of A depends on time. If the initial concentration of A and the rate constant k are known, the concentration of A at any time can be calculated.
2. Equation (12.2) is of the form $y = mx + b$, where a plot of y versus x is a straight line with slope m and intercept b . In Equation (12.2),

$$y = \ln[A] \quad x = t \quad m = -k \quad b = \ln[A]_0$$

For a first-order reaction, a plot of $\ln[A]$ versus t is always a straight line.

Thus, for a first-order reaction, plotting the natural logarithm of concentration versus time always gives a straight line. This fact is often used to test whether a reaction is first order. For the reaction



the reaction is first order in A if a plot of $\ln[A]$ versus t is a straight line. Conversely, if this plot is not a straight line, the reaction is not first order in A.

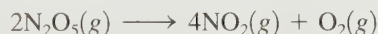
3. This integrated rate law for a first-order reaction also can be expressed in terms of a ratio of $[A]$ and $[A]_0$ as follows:

$$\ln\left(\frac{[A]_0}{[A]}\right) = kt$$

SAMPLE EXERCISE 12.2

First-Order Rate Laws I

The decomposition of N_2O_5 in the gas phase was studied at constant temperature.



The following results were collected:

$[\text{N}_2\text{O}_5]$ (mol/L)	Time (s)
0.1000	0
0.0707	50
0.0500	100
0.0250	200
0.0125	300
0.00625	400

Using these data, verify that the rate law is first order in $[\text{N}_2\text{O}_5]$, and calculate the value of the rate constant, where the rate $= -\Delta[\text{N}_2\text{O}_5]/\Delta t$.

SOLUTION

We can verify that the rate law is first order in $[\text{N}_2\text{O}_5]$ by constructing a plot of $\ln[\text{N}_2\text{O}_5]$ versus time. The values of $\ln[\text{N}_2\text{O}_5]$ at various times are given in the table on the next page, and the plot of $\ln[\text{N}_2\text{O}_5]$ versus time is shown in Fig. 12.4.

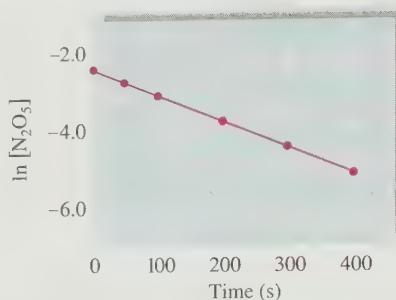


FIGURE 12.4

A plot of $\ln[\text{N}_2\text{O}_5]$ versus time.

$\ln[\text{N}_2\text{O}_5]$	Time (s)
-2.303	0
-2.649	50
-2.996	100
-3.689	200
-4.382	300
-5.075	400

The fact that the plot is a straight line confirms that the reaction is first order in N_2O_5 , since it follows the equation $\ln[\text{N}_2\text{O}_5] = -kt + \ln[\text{N}_2\text{O}_5]_0$.

Since the reaction is first order, the slope of the line equals $-k$, where

$$\text{Slope} = \frac{\text{change in } y}{\text{change in } x} = \frac{\Delta y}{\Delta x} = \frac{\Delta(\ln[\text{N}_2\text{O}_5])}{\Delta t}$$

Since the first and last points are exactly on the line, we will use these points to calculate the slope:

$$\text{Slope} = \frac{-5.075 - (-2.303)}{400. \text{ s} - 0 \text{ s}} = \frac{-2.772}{400. \text{ s}} = -6.93 \times 10^{-3} \text{ s}^{-1}$$

$$k = -(\text{slope}) = 6.93 \times 10^{-3} \text{ s}^{-1}$$

See Exercise 12.27.

SAMPLE EXERCISE 12.3

First-Order Rate Laws II

Using the data given in Sample Exercise 12.2, calculate $[\text{N}_2\text{O}_5]$ at 150 s after the start of the reaction.

SOLUTION

We know from Sample Exercise 12.2 that $[\text{N}_2\text{O}_5] = 0.0500 \text{ mol/L}$ at 100 s and $[\text{N}_2\text{O}_5] = 0.0250 \text{ mol/L}$ at 200 s. Since 150 s is halfway between 100 and 200 s, it is tempting to assume that we can simply use an arithmetic average to obtain $[\text{N}_2\text{O}_5]$ at that time. This is incorrect because it is $\ln[\text{N}_2\text{O}_5]$, not $[\text{N}_2\text{O}_5]$, that is directly proportional to t . To calculate $[\text{N}_2\text{O}_5]$ after 150 s, we use Equation (12.2):

$$\ln[\text{N}_2\text{O}_5] = -kt + \ln[\text{N}_2\text{O}_5]_0$$

where $t = 150. \text{ s}$, $k = 6.93 \times 10^{-3} \text{ s}^{-1}$ (as determined in Sample Exercise 12.2), and $[\text{N}_2\text{O}_5]_0 = 0.1000 \text{ mol/L}$.

$$\begin{aligned} \ln([\text{N}_2\text{O}_5])_{t=150} &= -(6.93 \times 10^{-3} \text{ s}^{-1})(150. \text{ s}) + \ln(0.100) \\ &= -1.040 - 2.303 = -3.343 \end{aligned}$$

$$[\text{N}_2\text{O}_5]_{t=150} = \text{antilog}(-3.343) = 0.0353 \text{ mol/L}$$

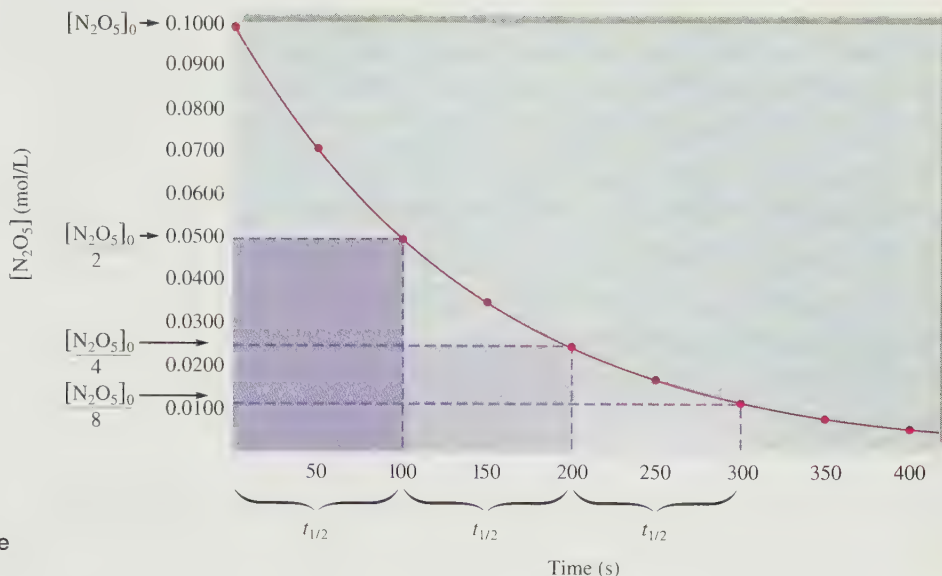
Note that this value of $[\text{N}_2\text{O}_5]$ is *not* halfway between 0.0500 and 0.0250 mol/L.

See Exercise 12.27.

The antilog operation means to exponentiate (see Appendix 1.2).

Half-Life of a First-Order Reaction

The time required for a reactant to reach half its original concentration is called the **half-life of a reactant** and is designated by the symbol $t_{1/2}$. For example, we

**FIGURE 12.5**

A plot of $[\text{N}_2\text{O}_5]$ versus time for the decomposition reaction of N_2O_5 .

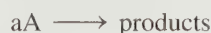
can calculate the half-life of the decomposition reaction discussed in Sample Exercise 12.2. The data plotted in Fig. 12.5 show that the half-life for this reaction is 100 seconds. We can see this by considering the following numbers:

$[\text{N}_2\text{O}_5](\text{mol/L})$	$t \text{ (s)}$
0.100	0
0.0500	100
0.0250	200
0.0125	300

$\Delta t = 100 \text{ s};$	$\frac{[\text{N}_2\text{O}_5]_{t=100}}{[\text{N}_2\text{O}_5]_{t=0}} = \frac{0.050}{0.100} = \frac{1}{2}$
$\Delta t = 100 \text{ s};$	$\frac{[\text{N}_2\text{O}_5]_{t=200}}{[\text{N}_2\text{O}_5]_{t=100}} = \frac{0.025}{0.050} = \frac{1}{2}$
$\Delta t = 100 \text{ s};$	$\frac{[\text{N}_2\text{O}_5]_{t=300}}{[\text{N}_2\text{O}_5]_{t=200}} = \frac{0.0125}{0.0250} = \frac{1}{2}$

Note that it *always* takes 100 seconds for $[\text{N}_2\text{O}_5]$ to be halved in this reaction.

A general formula for the half-life of a first-order reaction can be derived from the integrated rate law for the general reaction



If the reaction is first order in $[\text{A}]$,

$$\ln\left(\frac{[\text{A}]_0}{[\text{A}]}\right) = kt$$

By definition, when $t = t_{1/2}$,

$$[\text{A}] = \frac{[\text{A}]_0}{2}$$

Then, for $t = t_{1/2}$, the integrated rate law becomes

$$\ln\left(\frac{[A]_0}{[A]_0/2}\right) = kt_{1/2}$$

or

$$\ln(2) = kt_{1/2}$$

Substituting the value of $\ln(2)$ and solving for $t_{1/2}$ gives

$$t_{1/2} = \frac{0.693}{k} \quad (12.3)$$

For a first-order reaction, $t_{1/2}$ is independent of the initial concentration.

This is the *general equation for the half-life of a first-order reaction*. Equation (12.3) can be used to calculate $t_{1/2}$ if k is known or k if $t_{1/2}$ is known. Note that for a first-order reaction, *the half-life does not depend on concentration*.

SAMPLE EXERCISE 12.4

Half-Life for First-Order Reaction

A certain first-order reaction has a half-life of 20.0 minutes.

- Calculate the rate constant for this reaction.
- How much time is required for this reaction to be 75% complete?

SOLUTION

- Solving Equation (12.3) for k gives

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{20.0 \text{ min}} = 3.47 \times 10^{-2} \text{ min}^{-1}$$

- We use the integrated rate law in the form

$$\ln\left(\frac{[A]_0}{[A]}\right) = kt$$

If the reaction is 75% complete, 75% of the reactant has been consumed, leaving 25% in the original form:

$$\frac{[A]}{[A]_0} \times 100\% = 25\%$$

This means that

$$\frac{[A]}{[A]_0} = 0.25 \quad \text{or} \quad \frac{[A]_0}{[A]} = \frac{1}{0.25} = 4.0$$

$$\text{Then} \quad \ln\left(\frac{[A]_0}{[A]}\right) = \ln(4.0) = kt = \left(\frac{3.47 \times 10^{-2}}{\text{min}}\right)t$$

$$\text{and} \quad t = \frac{\ln(4.0)}{3.47 \times 10^{-2} \text{ min}} = 40. \text{ min}$$

Thus it takes 40. minutes for this particular reaction to reach 75% completion.

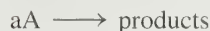
Let's consider another way of solving this problem using the definition of half-life. After one half-life the reaction has gone 50% to completion. If the initial concentration were 1.0 mol/L, after one half-life the concentration would be

0.50 mol/L. One more half-life would produce a concentration of 0.25 mol/L. Comparing 0.25 mol/L with the original 1.0 mol/L shows that 25% of the reactant is left after two half-lives. This is a general result. (What percentage of reactant remains after three half-lives?) Two half-lives for this reaction is 2(20.0 min), or 40.0 min, which agrees with the preceding answer.

See Exercises 12.28 and 12.38 through 12.40.

Second-Order Rate Laws

For a general reaction involving a single reactant, that is,



that is second order in A, the rate law is

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]^2 \quad (12.4)$$

The **integrated second-order rate law** has the form

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0} \quad (12.5)$$

Note the following characteristics of Equation (12.5):

1. A plot of $1/[A]$ versus t will produce a straight line with a slope equal to k .
2. Equation (12.5) shows how $[A]$ depends on time and can be used to calculate $[A]$ at any time t , provided k and $[A]_0$ are known.

When one half-life of the second-order reaction has elapsed ($t = t_{1/2}$), by definition,

$$[A] = \frac{[A]_0}{2}$$

Equation (12.5) then becomes

$$\begin{aligned} \frac{1}{\frac{[A]_0}{2}} &= kt_{1/2} + \frac{1}{[A]_0} \\ \frac{2}{[A]_0} - \frac{1}{[A]_0} &= kt_{1/2} \\ \frac{1}{[A]_0} &= kt_{1/2} \end{aligned}$$

Solving for $t_{1/2}$ gives the expression for the half-life of a second-order reaction:

$$t_{1/2} = \frac{1}{k[A]_0} \quad (12.6)$$

Second order: $\text{rate} = k[A]^2$. Doubling the concentration of A quadruples the reaction rate; tripling the concentration of A increases the rate by nine times.

For second-order reactions, a plot of $1/[A]$ versus t will be linear.

SAMPLE EXERCISE 12.5

When two identical molecules combine, the resulting molecule is called a *dimer*.

Determining Rate Laws

Butadiene reacts to form its dimer according to the equation



The following data were collected for this reaction at a given temperature:

$[\text{C}_4\text{H}_6]$ (mol/L)	Time (± 1 s)
0.01000	0
0.00625	1000
0.00476	1800
0.00370	2800
0.00313	3600
0.00270	4400
0.00241	5200
0.00208	6200

- Is this reaction first order or second order?
- What is the value of the rate constant for the reaction?
- What is the half-life for the reaction under the conditions of this experiment?

SOLUTION

- To decide whether the rate law for this reaction is first order or second order, we must see whether the plot of $\ln[\text{C}_4\text{H}_6]$ versus time is a straight line (first order) or the plot of $1/[\text{C}_4\text{H}_6]$ versus time is a straight line (second order). The data necessary to make these plots are as follows:

t (s)	$\frac{1}{[\text{C}_4\text{H}_6]}$	$\ln[\text{C}_4\text{H}_6]$
0	100	-4.605
1000	160	-5.075
1800	210	-5.348
2800	270	-5.599
3600	320	-5.767
4400	370	-5.915
5200	415	-6.028
6200	481	-6.175

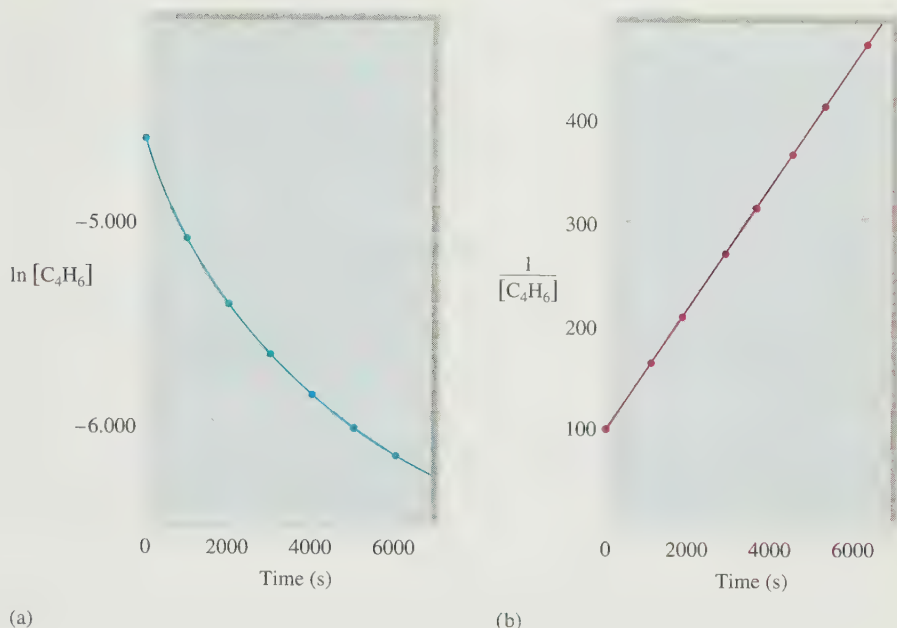
The resulting plots are shown in Fig. 12.6. Since the $\ln[\text{C}_4\text{H}_6]$ versus t plot [Fig. 12.6(a)] is not a straight line, the reaction is *not* first order. The reaction is, however, second order, as shown by the linearity of the $1/[\text{C}_4\text{H}_6]$ versus t plot [Fig. 12.6(b)]. Thus we can now write the rate law for this second-order reaction:

$$\text{Rate} = -\frac{\Delta[\text{C}_4\text{H}_6]}{\Delta t} = k[\text{C}_4\text{H}_6]^2$$

- For a second-order reaction, a plot of $1/[\text{C}_4\text{H}_6]$ versus t produces a straight line of slope k . In terms of the standard equation for a straight line, $y = mx + b$, we have $y = 1/[\text{C}_4\text{H}_6]$ and $x = t$. Thus the slope of the line can be expressed as follows:

$$\text{Slope} = \frac{\Delta y}{\Delta x} = \frac{\Delta\left(\frac{1}{[\text{C}_4\text{H}_6]}\right)}{\Delta t}$$

Butadiene (C_4H_6) and its dimer (C_8H_{12}).

**FIGURE 12.6**(a) A plot of $\ln[C_4H_6]$ versus t .(b) A plot of $1/[C_4H_6]$ versus t .

Using the points at $t = 0$ and $t = 6200$, we can find the rate constant for the reaction:

$$k = \text{slope} = \frac{(481 - 100) \text{ L/mol}}{(6200. - 0) \text{ s}} = \frac{381}{6200.} \text{ L/mol} \cdot \text{s} = 6.14 \times 10^{-2} \text{ L/mol} \cdot \text{s}$$

c. The expression for the half-life of a second-order reaction is

$$t_{1/2} = \frac{1}{k[A]_0}$$

In this case $k = 6.14 \times 10^{-2} \text{ L/mol} \cdot \text{s}$ (from part b) and $[A]_0 = [C_4H_6]_0 = 0.01000 \text{ M}$ (the concentration at $t = 0$). Thus

$$t_{1/2} = \frac{1}{(6.14 \times 10^{-2} \text{ L/mol} \cdot \text{s})(1.000 \times 10^{-2} \text{ mol/L})} = 1.63 \times 10^3 \text{ s}$$

The initial concentration of C_4H_6 is halved in 1630 s.

See Exercises 12.29, 12.30, 12.41, and 12.42.

For a second-order reaction, $t_{1/2}$ is dependent on $[A]_0$. For a first-order reaction, $t_{1/2}$ is independent of $[A]_0$.

It is important to recognize the difference between the half-life for a first-order reaction and the half-life for a second-order reaction. For a second-order reaction, $t_{1/2}$ depends on both k and $[A]_0$; for a first-order reaction, $t_{1/2}$ depends only on k . For a first-order reaction, a constant time is required to reduce the concentration of the reactant by half, and then by half again, and so on, as the reaction proceeds. From Sample Exercise 12.5 we can see that this is *not* true for a second-order reaction. For that second-order reaction, we found that the first half-life (the time required to go from $[C_4H_6] = 0.010 \text{ M}$ to $[C_4H_6] = 0.0050 \text{ M}$) is 1630 seconds. We can estimate the second half-life from the concentration data as a function of time. Note that to reach $0.0024 \text{ M } C_4H_6$ (approximately $0.0050/2$) requires 5200 seconds of reaction time. Thus to get from $0.0050 \text{ M } C_4H_6$ to $0.0024 \text{ M } C_4H_6$ takes 3570

For each successive half-life, $[A]_0$ is halved. Since $t_{1/2} = 1/k[A]_0$, $t_{1/2}$ doubles.

seconds (5200 – 1630). The second half-life is much longer than the first. This pattern is characteristic of second-order reactions. In fact, *for a second-order reaction, each successive half-life is double the preceding one* (provided the effects of the reverse reaction can be ignored, as we are assuming here). Prove this to yourself by examining the equation $t_{1/2} = 1/(k[A]_0)$.

Zero-Order Rate Laws

Most reactions involving a single reactant show either first-order or second-order kinetics. However, sometimes such a reaction can be a **zero-order reaction**. The rate law for a zero-order reaction is

$$\text{Rate} = k[A]^0 = k(1) = k$$

For a zero-order reaction, the rate is constant. It does not change with concentration as it does for first-order or second-order reactions.

The **integrated rate law for a zero-order reaction** is

$$[A] = -kt + [A]_0 \quad (12.7)$$

In this case a plot of $[A]$ versus t gives a straight line of slope $-k$, as shown in Fig. 12.7.

The expression for the half-life of a zero-order reaction can be obtained from the integrated rate law. By definition, $[A] = [A]_0/2$ when $t = t_{1/2}$, so

$$\frac{[A]_0}{2} = -kt_{1/2} + [A]_0$$

or

$$kt_{1/2} = \frac{[A]_0}{2k}$$

Solving for $t_{1/2}$ gives

$$t_{1/2} = \frac{[A]_0}{2k} \quad (12.8)$$

Zero-order reactions are most often encountered when a substance such as a metal surface or an enzyme is required for the reaction to occur. For example, the decomposition reaction



occurs on a hot platinum surface. When the platinum surface is completely covered with N_2O molecules, an increase in the concentration of N_2O has no effect on the rate, since only those N_2O molecules on the surface can react. Under these conditions, *the rate is a constant* because it is controlled by what happens on the platinum surface rather than by the total concentration of N_2O , as illustrated in Fig. 12.8. This reaction also can occur at high temperatures with no platinum surface present, but under these conditions, it is not zero order.

Integrated Rate Laws for Reactions with More Than One Reactant

So far we have considered the integrated rate laws for simple reactions with only one reactant. Special techniques are required to deal with more complicated reactions. Let's consider the reaction

A zero-order reaction has a constant rate.

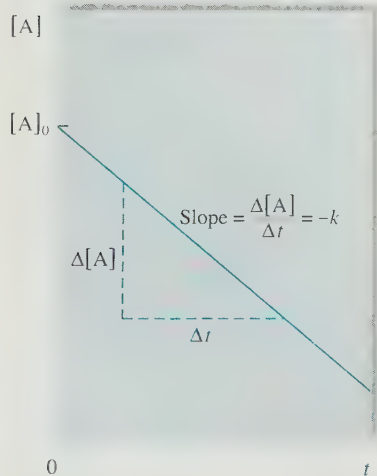
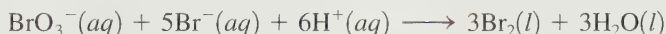
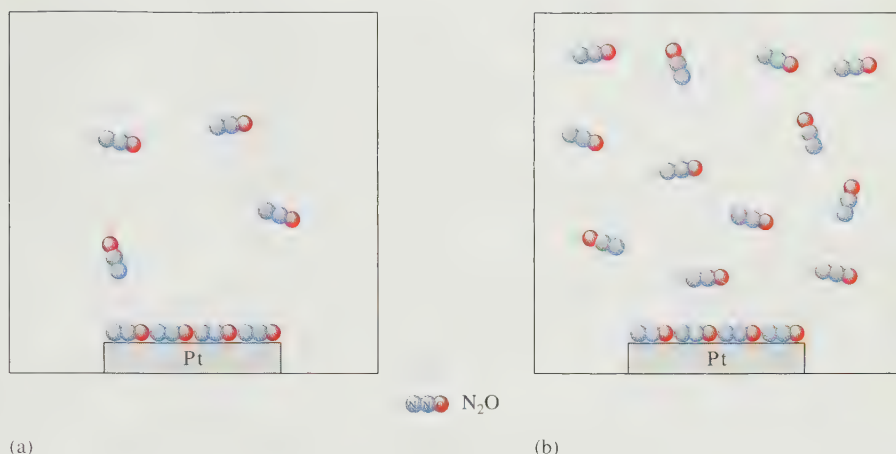


FIGURE 12.7
A plot of $[A]$ versus t for a zero-order reaction.

FIGURE 12.8

The decomposition reaction $2\text{N}_2\text{O}(g) \rightarrow 2\text{N}_2(g) + \text{O}_2(g)$ takes place on a platinum surface. Although $[\text{N}_2\text{O}]$ is twice as great in (b) as in (a), the rate of decomposition of N_2O is the same in both cases because the platinum surface can accommodate only a certain number of molecules. As a result, this reaction is zero order.



From experimental evidence we know that the rate law is

$$\text{Rate} = -\frac{\Delta[\text{BrO}_3^-]}{\Delta t} = k[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2$$

Suppose we run this reaction under conditions where $[\text{BrO}_3^-]_0 = 1.0 \times 10^{-3} M$, $[\text{Br}^-]_0 = 1.0 M$, and $[\text{H}^+]_0 = 1.0 M$. As the reaction proceeds, $[\text{BrO}_3^-]$ decreases significantly, but because the Br^- ion and H^+ ion concentrations are so large initially, relatively little of these two reactants is consumed. Thus $[\text{Br}^-]$ and $[\text{H}^+]$ remain *approximately constant*. In other words, under the conditions where the Br^- ion and H^+ ion concentrations are much larger than the BrO_3^- ion concentration, we can assume that throughout the reaction

$$[\text{Br}^-] = [\text{Br}^-]_0 \quad \text{and} \quad [\text{H}^+] = [\text{H}^+]_0$$

This means that the rate law can be written

$$\text{Rate} = k[\text{Br}^-]_0[\text{H}^+]_0^2[\text{BrO}_3^-] = k'[\text{BrO}_3^-]$$

where, since $[\text{Br}^-]_0$ and $[\text{H}^+]_0$ are constant,

$$k' = k[\text{Br}^-]_0[\text{H}^+]_0^2$$

The rate law

$$\text{Rate} = k'[\text{BrO}_3^-]$$

is first order. However, since this law was obtained by simplifying a more complicated one, it is called a **pseudo-first-order rate law**. Under the conditions of this experiment, a plot of $\ln[\text{BrO}_3^-]$ versus t will give a straight line where the slope is equal to $-k'$. Since $[\text{Br}^-]_0$ and $[\text{H}^+]_0$ are known, the value of k can be calculated from the equation

$$k' = k[\text{Br}^-]_0[\text{H}^+]_0^2$$

which can be rearranged to give

$$k = \frac{k'}{[\text{Br}^-]_0[\text{H}^+]_0^2}$$

Note that the kinetics of complicated reactions can be studied by observing the behavior of one reactant at a time. If the concentration of one reactant is much smaller than the concentrations of the others, then the amounts of those reactants present in large concentrations will not change significantly and can be regarded as constant. The change in concentration with time of the reactant present in a relatively small amount can then be used to determine the order of the reaction in that component. This technique allows us to determine rate laws for complex reactions.

12.5 Rate Laws: A Summary

In the last several sections we have developed the following important points:

1. To simplify the rate laws for reactions, we have always assumed that the rate is being studied under conditions where only the forward reaction is important. This produces rate laws that contain only reactant concentrations.
2. There are two types of rate laws.
 - a. The *differential rate law* (often called the *rate law*) shows how the rate depends on the concentrations. The forms of the rate laws for zero-order, first-order, and second-order kinetics of reactions with single reactants are shown in Table 12.6.
 - b. The *integrated rate law* shows how concentration depends on time. The integrated rate laws corresponding to zero-order, first-order, and second-order kinetics of one-reactant reactions are given in Table 12.6.
3. Whether we determine the differential rate law or the integrated rate law depends on the type of data that can be collected conveniently and accurately. Once we have experimentally determined either type of rate law, we can write the other for a given reaction.
4. The most common method for experimentally determining the differential rate law is the method of initial rates. In this method several experiments are run at different initial concentrations and the instantaneous rates are determined for each at the same value of t (as close to $t = 0$ as possible). The point is to eval-

TABLE 12.6 Summary of the Kinetics for Reactions of the Type $aA \rightarrow$ Products That Are Zero, First, or Second Order in $[A]$

	Order		
	Zero	First	Second
Rate Law:	Rate = k	Rate = $k[A]$	Rate = $k[A]^2$
Integrated Rate Law:	$[A] = -kt + [A]_0$	$\ln[A] = -kt + \ln[A]_0$	$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$
Plot Needed to Give a Straight Line:	$[A]$ versus t	$\ln[A]$ versus t	$\frac{1}{[A]}$ versus t
Relationship of Rate Constant to the Slope of Straight Line:	Slope = $-k$	Slope = $-k$	Slope = k
Half-life:	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$

uate the rate before the concentrations change significantly from the initial values. From a comparison of the initial rates and the initial concentrations the dependence of the rate on the concentrations of various reactants can be obtained—that is, the order in each reactant can be determined.

5. To experimentally determine the integrated rate law for a reaction, concentrations are measured at various values of t as the reaction proceeds. Then the job is to see which integrated rate law correctly fits the data. Typically this is done visually by ascertaining which type of plot gives a straight line. A summary for one-reactant reactions is given in Table 12.6. Once the correct straight-line plot is found, the correct integrated rate law can be chosen and the value of k obtained from the slope. Also, the (differential) rate law for the reaction can then be written.
6. The integrated rate law for a reaction that involves several reactants can be treated by choosing conditions such that the concentration of only one reactant varies in a given experiment. This is done by having the concentration of one reactant remain small compared with the concentrations of all the others, causing a rate law such as

$$\text{Rate} = k[\text{A}]^n[\text{B}]^m[\text{C}]^p$$

to reduce to

$$\text{Rate} = k'[\text{A}]^n$$

where $k' = k[\text{B}]_0^m[\text{C}]_0^p$ and $[\text{B}]_0 \gg [\text{A}]_0$ and $[\text{C}]_0 \gg [\text{A}]_0$. The value of n is obtained by determining whether a plot of $[\text{A}]$ versus t is linear ($n = 0$), a plot of $\ln[\text{A}]$ versus t is linear ($n = 1$), or a plot of $1/[\text{A}]$ versus t is linear ($n = 2$). The value of k' is determined from the slope of the appropriate plot. The values of m , p , and k can be found by determining the value of k' at several different concentrations of B and C.

12.6 Reaction Mechanisms

Most chemical reactions occur by a *series of steps* called the **reaction mechanism**. To understand a reaction, we must know its mechanism, and one of the main purposes for studying kinetics is to learn as much as possible about the steps involved in a reaction. In this section we explore some of the fundamental characteristics of reaction mechanisms.

Consider the reaction between nitrogen dioxide and carbon monoxide:



The rate law for this reaction is known from experiment to be

$$\text{Rate} = k[\text{NO}_2]^2$$

As we will see below, this reaction is more complicated than it appears from the balanced equation. This is quite typical; the balanced equation for a reaction tells us the reactants, the products, and the stoichiometry but gives no direct information about the reaction mechanism.

For the reaction between nitrogen dioxide and carbon monoxide, the mechanism is thought to involve the following steps:

A balanced equation does not tell us *how* the reactants become products.

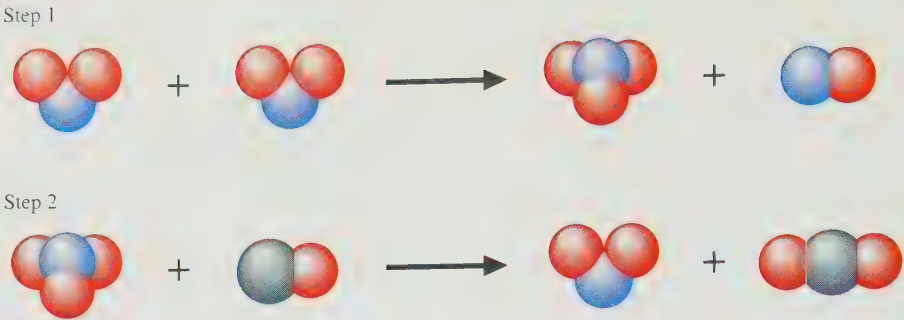
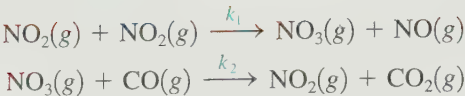


FIGURE 12.9
A molecular representation of the elementary steps in the reaction of NO₂ and CO.

An intermediate is formed in one step and used up in a subsequent step and so is never seen as a product.

The prefix *uni-* means one, *bi-* means two, and *ter-* means three.

A unimolecular elementary step is always first order, a bimolecular step is always second order, and so on.



where k_1 and k_2 are the rate constants of the individual reactions. In this mechanism, gaseous NO₃ is an **intermediate**, a species that is neither a reactant nor a product but that is formed and consumed during the reaction sequence. This reaction is illustrated in Fig. 12.9.

Each of these two reactions is called an **elementary step**, a reaction whose rate law can be written from its molecularity. **Molecularity** is defined as the number of species that must collide to produce the reaction indicated by that step. A reaction involving one molecule is called a **unimolecular step**. Reactions involving the collision of two and three species are termed **bimolecular** and **termolecular**, respectively. Termolecular steps are quite rare, because the probability of three molecules colliding simultaneously is very small. Examples of these three types of elementary steps and the corresponding rate laws are shown in Table 12.7. Note from Table 12.7 that the rate law for an elementary step follows *directly* from the molecularity of that step. For example, for a bimolecular step the rate law is always second order, either of the form $k[A]^2$ for a step with a single reactant or of the form $k[A][B]$ for a step involving two reactants.

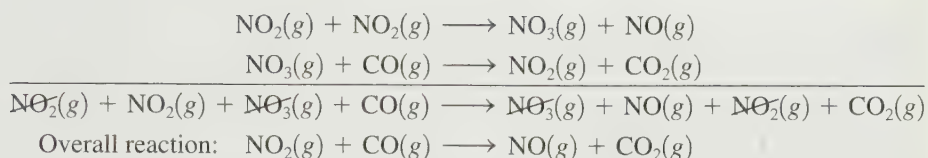
We can now define a reaction mechanism more precisely. It is a *series of elementary steps that must satisfy two requirements*:

1. The sum of the elementary steps must give the overall balanced equation for the reaction.
2. The mechanism must agree with the experimentally determined rate law.

To see how these requirements are applied, we will consider the mechanism given above for the reaction of nitrogen dioxide and carbon monoxide. First, note that the sum of the two steps gives the overall balanced equation:

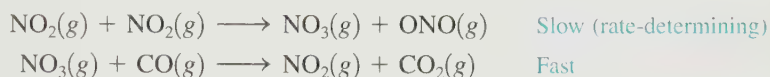
TABLE 12.7 Examples of Elementary Steps

Elementary Step	Molecularity	Rate Law
A → products	Unimolecular	Rate = $k[A]$
A + A → products (2A → products)	Bimolecular	Rate = $k[A]^2$
A + B → products	Bimolecular	Rate = $k[A][B]$
A + A + B → products (2A + B → products)	Termolecular	Rate = $k[A]^2[B]$
A + B + C → products	Termolecular	Rate = $k[A][B][C]$



The first requirement for a correct mechanism is met. To see whether the mechanism meets the second requirement, we need to introduce a new idea: the **rate-determining step**. Multistep reactions often have one step that is much slower than all the others. Reactants can become products only as fast as they can get through this slowest step. That is, the overall reaction can be no faster than the slowest, or rate-determining, step in the sequence. An analogy for this situation is the pouring of water rapidly into a container through a funnel. The water collects in the container at a rate that is essentially determined by the size of the funnel opening and not by the rate of pouring.

Which is the rate-determining step in the reaction of nitrogen dioxide and carbon monoxide? Let's *assume* that the first step is rate-determining and the second step is relatively fast:



What we have really assumed here is that the formation of NO_3 occurs much more slowly than its reaction with CO . The rate of CO_2 production is then controlled by the rate of formation of NO_3 in the first step. Since this is an elementary step, we can write the rate law from the molecularity. The bimolecular first step has the rate law

$$\text{Rate of formation of NO}_3 = \frac{\Delta[\text{NO}_3]}{\Delta t} = k_1[\text{NO}_2]^2$$

Since the overall reaction rate can be no faster than the slowest step,

$$\text{Overall rate} = k_1[\text{NO}_2]^2$$

Note that this rate law agrees with the experimentally determined rate law given earlier. The mechanism we assumed above satisfies the two requirements stated earlier and *may* be the correct mechanism for the reaction.

How does a chemist deduce the mechanism for a given reaction? The rate law is always determined first. Then, using chemical intuition and following the two rules given on the previous page, the chemist constructs possible mechanisms and tries, with further experiments, to eliminate those that are least likely. *A mechanism can never be proved absolutely.* We can only say that a mechanism that satisfies the two requirements is *possibly* correct. Deducing mechanisms for chemical reactions can be difficult and requires skill and experience. We will only touch on this process in this text.

A reaction is only as fast as its slowest step.

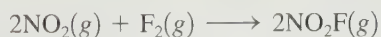


Visualization: Oscillating Reaction

SAMPLE EXERCISE 12.6

Reaction Mechanisms

The balanced equation for the reaction of the gases nitrogen dioxide and fluorine is

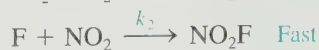


The experimentally determined rate law is

$$\text{Rate} = k[\text{NO}_2][\text{F}_2]$$



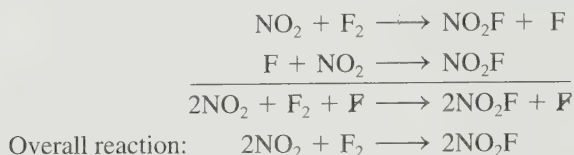
A suggested mechanism for this reaction is



Is this an acceptable mechanism? That is, does it satisfy the two requirements?

SOLUTION

The first requirement for an acceptable mechanism is that the sum of the steps should give the balanced equation:



The first requirement is met.

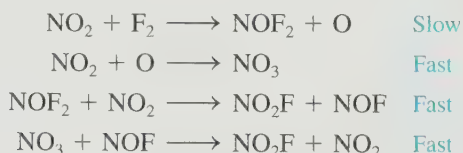
The second requirement is that the mechanism must agree with the experimentally determined rate law. Since the proposed mechanism states that the first step is rate-determining, the overall reaction rate must be that of the first step. The first step is bimolecular, so the rate law is

$$\text{Rate} = k_1[\text{NO}_2][\text{F}_2]$$

This has the same form as the experimentally determined rate law. The proposed mechanism is acceptable because it satisfies both requirements. (Note that we have not proved that it is *the correct* mechanism.)

See Exercises 12.47 and 12.48.

Although the mechanism given in Sample Exercise 12.6 has the correct stoichiometry and fits the observed rate law, other mechanisms may also satisfy these requirements. For example, the mechanism might be



To decide on the most probable mechanism for the reaction, the chemist doing the study would have to perform additional experiments.



Understanding Concepts:
Transition States and Activation Energy

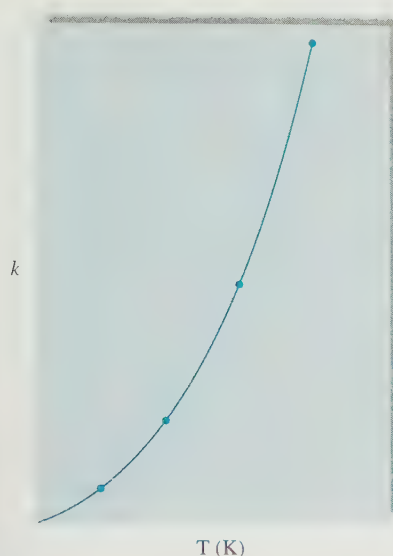
12.7 A Model for Chemical Kinetics

How do chemical reactions occur? We already have given some indications. For example, we have seen that the rates of chemical reactions depend on the concentrations of the reacting species. The initial rate for the reaction



can be described by the rate law

$$\text{Rate} = k[\text{A}]^n[\text{B}]^m$$

**FIGURE 12.10**

A plot showing the exponential dependence of the rate constant on absolute temperature. The exact temperature dependence of k is different for each reaction. This plot represents the behavior of a rate constant that doubles for every increase in temperature of 10 K.

The higher the activation energy, the slower is the reaction at a given temperature.

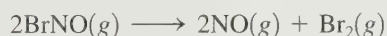
where the order of each reactant depends on the detailed reaction mechanism. This explains why reaction rates depend on concentration. But what about some of the other factors affecting reaction rates? For example, how does temperature affect the speed of a reaction?

We can answer this question qualitatively from our experience. We have refrigerators because food spoilage is retarded at low temperatures. The combustion of wood occurs at a measurable rate only at high temperatures. An egg cooks in boiling water much faster at sea level than in Leadville, Colorado (elevation 10,000 ft), where the boiling point of water is approximately 90°C. These observations and others lead us to conclude that *chemical reactions speed up when the temperature is increased*. Experiments have shown that virtually all rate constants show an exponential increase with absolute temperature, as represented in Fig. 12.10.

In this section we discuss a model used to account for the observed characteristics of reaction rates. This model, called the **collision model**, is built around the central idea that *molecules must collide to react*. We have already seen how this assumption explains the concentration dependence of reaction rates. Now we need to consider whether this model can account for the observed temperature dependence of reaction rates.

The kinetic molecular theory of gases predicts that an increase in temperature raises molecular velocities and so increases the frequency of collisions between molecules. This idea agrees with the observation that reaction rates are greater at higher temperatures. Thus there is qualitative agreement between the collision model and experimental observations. However, it is found that the rate of reaction is much smaller than the calculated collision frequency in a collection of gas particles. This must mean that *only a small fraction of the collisions produces a reaction*. Why?

This question was first addressed in the 1880s by Svante Arrhenius. He proposed the existence of a *threshold energy*, called the **activation energy**, that must be overcome to produce a chemical reaction. Such a proposal makes sense, as we can see by considering the decomposition of BrNO in the gas phase:

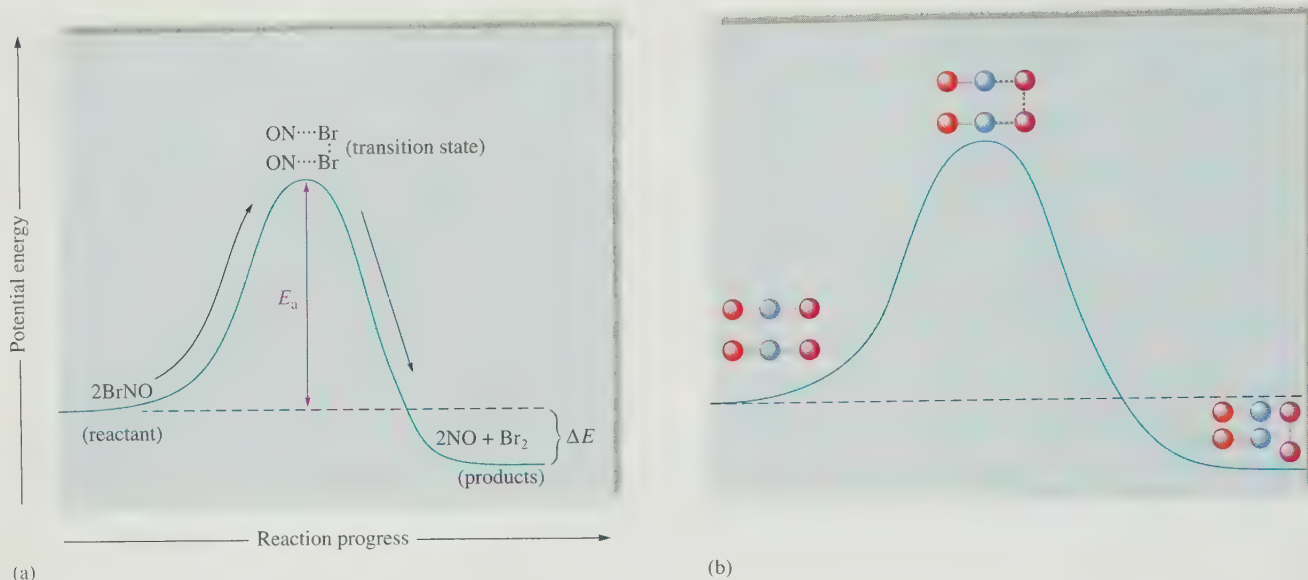


In this reaction two Br—N bonds must be broken and one Br—Br bond must be formed. Breaking a Br—N bond requires considerable energy (243 kJ/mol), which must come from somewhere. The collision model postulates that the energy comes from the kinetic energies possessed by the reacting molecules before the collision. This kinetic energy is changed into potential energy as the molecules are distorted during a collision to break bonds and rearrange the atoms into the product molecules.

We can envision the reaction progress as shown in Fig. 12.11. The arrangement of atoms found at the top of the potential energy “hill,” or barrier, is called the **activated complex**, or **transition state**. The conversion of BrNO to NO and Br₂ is exothermic, as indicated by the fact that the products have lower potential energy than the reactant. However, ΔE has no effect on the rate of the reaction. Rather, the rate depends on the size of the activation energy E_a .

The main point here is that a certain minimum energy is required for two BrNO molecules to “get over the hill” so that products can form. This energy is furnished by the energy of the collision. A collision between two BrNO molecules with small kinetic energies will not have enough energy to get over the barrier. At a given temperature only a certain fraction of the collisions possesses enough energy to be effective (to result in product formation).

We can be more precise by recalling from Chapter 5 that a distribution of velocities exists in a sample of gas molecules. Therefore, a distribution of collision

**FIGURE 12.11**

(a) The change in potential energy as a function of reaction progress for the reaction $2\text{BrNO} \rightarrow 2\text{NO} + \text{Br}_2$. The activation energy E_a represents the energy needed to disrupt the BrNO molecules so that they can form products. The quantity ΔE represents the net change in energy in going from reactant to products. (b) A molecular representation of the reaction.

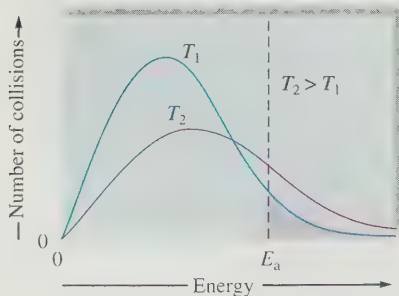
energies also exists, as shown in Fig. 12.12 for two different temperatures. Figure 12.12 also shows the activation energy for the reaction in question. Only collisions with energy greater than the activation energy are able to react (get over the barrier). At the lower temperature, T_1 , the fraction of effective collisions is quite small. However, as the temperature is increased to T_2 , the fraction of collisions with the required activation energy increases dramatically. When the temperature is doubled, the fraction of effective collisions much more than doubles. In fact, the fraction of effective collisions increases *exponentially* with temperature. This is encouraging for our theory; remember that rates of reactions are observed to increase exponentially with temperature. Arrhenius postulated that the number of collisions having an energy greater than or equal to the activation energy is given by the expression:

$$\text{Number of collisions with the activation energy} = (\text{total number of collisions})e^{-E_a/RT}$$

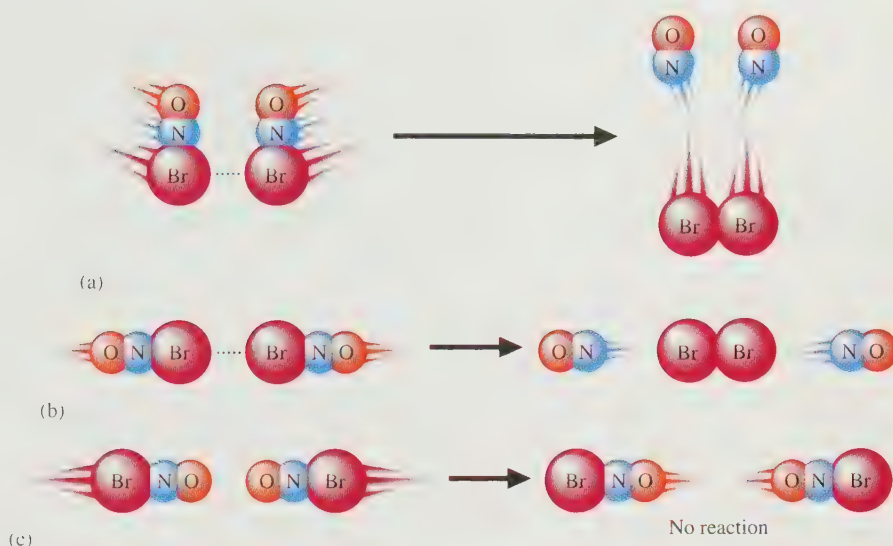
where E_a is the activation energy, R is the universal gas constant, and T is the Kelvin temperature. The factor $e^{-E_a/RT}$ represents the fraction of collisions with energy E_a or greater at temperature T .

We have seen that not all molecular collisions are effective in producing chemical reactions because a minimum energy is required for the reaction to occur. There is, however, another complication. Experiments show that the *observed reaction rate is considerably smaller than the rate of collisions with enough energy to surmount the barrier*. This means that many collisions, even though they have the required energy, still do not produce a reaction. Why not?

The answer lies in the **molecular orientations** during collisions. We can illustrate this using the reaction between two BrNO molecules, as shown in Fig. 12.13.

**FIGURE 12.12**

Plot showing the number of collisions with a particular energy at T_1 and T_2 , where $T_2 > T_1$.

**FIGURE 12.13**

Several possible orientations for a collision between two BrNO molecules. Orientations (a) and (b) can lead to a reaction, but orientation (c) cannot.

Some collision orientations can lead to reaction, and others cannot. Therefore, we must include a correction factor to allow for collisions with nonproductive molecular orientations.

To summarize, two requirements must be satisfied for reactants to collide successfully (to rearrange to form products):

1. The collision must involve enough energy to produce the reaction; that is, the collision energy must equal or exceed the activation energy.
2. The relative orientation of the reactants must allow formation of any new bonds necessary to produce products.

Taking these factors into account, we can represent the rate constant as

$$k = zp e^{-E_a/RT}$$

where z is the collision frequency, p is called the **steric factor** (always less than 1) and reflects the fraction of collisions with effective orientations, and $e^{-E_a/RT}$ represents the fraction of collisions with sufficient energy to produce a reaction. This expression is most often written in form

$$k = A e^{-E_a/RT} \quad (12.9)$$

which is called the **Arrhenius equation**. In this equation, A replaces zp and is called the **frequency factor** for the reaction.

Taking the natural logarithm of each side of the Arrhenius equation gives

$$\ln(k) = -\frac{E_a}{R} \left(\frac{1}{T} \right) + \ln(A) \quad (12.10)$$

Equation (12.10) is a linear equation of the type $y = mx + b$, where $y = \ln(k)$, $m = -E_a/R = \text{slope}$, $x = 1/T$, and $b = \ln(A) = \text{intercept}$. Thus, for a reaction where the rate constant obeys the Arrhenius equation, a plot of $\ln(k)$ versus $1/T$ gives a



A snowy tree cricket. The frequency of a cricket's chirps depends on the temperature of the cricket.

straight line. The slope and intercept can be used to determine, respectively, the values of E_a and A characteristic of that reaction. The fact that most rate constants obey the Arrhenius equation to a good approximation indicates that the collision model for chemical reactions is physically reasonable.

SAMPLE EXERCISE 12.7

Determining Activation Energy I

The reaction



was studied at several temperatures, and the following values of k were obtained:

$k \text{ (s}^{-1}\text{)}$	$T \text{ (}^\circ\text{C)}$
2.0×10^{-5}	20
7.3×10^{-5}	30
2.7×10^{-4}	40
9.1×10^{-4}	50
2.9×10^{-3}	60

Calculate the value of E_a for this reaction.

SOLUTION

To obtain the value of E_a , we need to construct a plot of $\ln(k)$ versus $1/T$. First, we must calculate values of $\ln(k)$ and $1/T$, as shown below:

$T \text{ (}^\circ\text{C)}$	$T \text{ (K)}$	$1/T \text{ (K}^{-1}\text{)}$	$k \text{ (s}^{-1}\text{)}$	$\ln(k)$
20	293	3.41×10^{-3}	2.0×10^{-5}	-10.82
30	303	3.30×10^{-3}	7.3×10^{-5}	-9.53
40	313	3.19×10^{-3}	2.7×10^{-4}	-8.22
50	323	3.10×10^{-3}	9.1×10^{-4}	-7.00
60	333	3.00×10^{-3}	2.9×10^{-3}	-5.84

The plot of $\ln(k)$ versus $1/T$ is shown in Fig. 12.14, where the slope

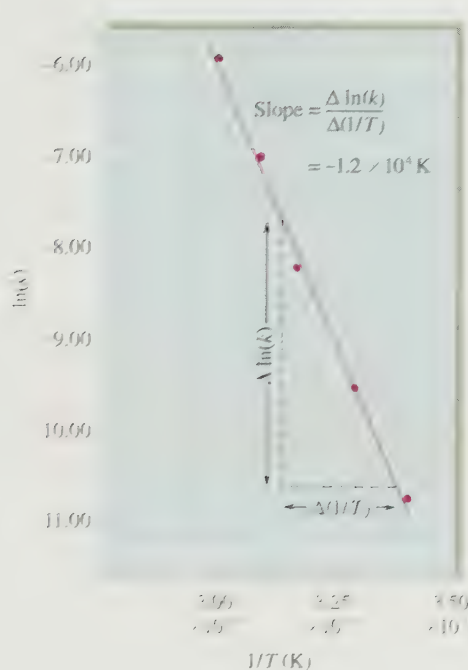
$$\frac{\Delta \ln(k)}{\Delta \left(\frac{1}{T} \right)}$$

is found to be $-1.2 \times 10^4 \text{ K}$. The value of E_a can be determined by solving the following equation:

$$\begin{aligned} \text{Slope} &= -\frac{E_a}{R} \\ E_a &= -R(\text{slope}) = -(8.3145 \text{ J/K} \cdot \text{mol})(-1.2 \times 10^4 \text{ K}) \\ &= 1.0 \times 10^5 \text{ J/mol} \end{aligned}$$

Thus the value of the activation energy for this reaction is $1.0 \times 10^5 \text{ J/mol}$.

See Exercises 12.53 and 12.54.

**FIGURE 12.14**

Plot of $\ln(k)$ versus $1/T$ for the reaction $2\text{N}_2\text{O}_5(\text{g}) \rightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$. The value of the activation energy for this reaction can be obtained from the slope of the line, which equals $-E_a/R$.

The most common procedure for finding E_a for a reaction involves measuring the rate constant k at several temperatures and then plotting $\ln(k)$ versus $1/T$, as shown in Sample Exercise 12.7. However, E_a also can be calculated from the values of k at only two temperatures by using a formula that can be derived as follows from Equation (12.10).

At temperature T_1 , where the rate constant is k_1 ,

$$\ln(k_1) = -\frac{E_a}{RT_1} + \ln(A)$$

At temperature T_2 , where the rate constant is k_2 ,

$$\ln(k_2) = -\frac{E_a}{RT_2} + \ln(A)$$

Subtracting the first equation from the second gives

$$\begin{aligned} \ln(k_2) - \ln(k_1) &= \left[-\frac{E_a}{RT_2} + \ln(A) \right] - \left[-\frac{E_a}{RT_1} + \ln(A) \right] \\ &= -\frac{E_a}{RT_2} + \frac{E_a}{RT_1} \end{aligned}$$

And

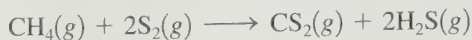
$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (12.11)$$

Therefore, the values of k_1 and k_2 measured at temperatures T_1 and T_2 can be used to calculate E_a , as shown in Sample Exercise 12.8.

SAMPLE EXERCISE 12.8

Determining Activation Energy II

The gas-phase reaction between methane and diatomic sulfur is given by the equation



At 550°C the rate constant for this reaction is 1.1 L/mol · s, and at 625°C the rate constant is 6.4 L/mol · s. Using these values, calculate E_a for this reaction.

SOLUTION

The relevant data are shown in the following table:

k (L/mol · s)	T (°C)	T (K)
1.1 = k_1	550	823 = T_1
6.4 = k_2	625	898 = T_2

Substituting these values into Equation (12.11) gives

$$\ln\left(\frac{6.4}{1.1}\right) = \frac{E_a}{8.3145 \text{ J/K} \cdot \text{mol}} \left(\frac{1}{823 \text{ K}} - \frac{1}{898 \text{ K}} \right)$$

Solving for E_a gives

$$\begin{aligned} E_a &= \frac{(8.3145 \text{ J/K} \cdot \text{mol}) \ln\left(\frac{6.4}{1.1}\right)}{\left(\frac{1}{823 \text{ K}} - \frac{1}{898 \text{ K}}\right)} \\ &= 1.4 \times 10^5 \text{ J/mol} \end{aligned}$$

See Exercises 12.55 through 12.58.

12.8 Catalysis

We have seen that the rate of a reaction increases dramatically with temperature. If a particular reaction does not occur fast enough at normal temperatures, we can speed it up by raising the temperature. However, sometimes this is not feasible. For example, living cells can survive only in a rather narrow temperature range, and the human body is designed to operate at an almost constant temperature of 98.6°F. But many of the complicated biochemical reactions keeping us alive would be much too slow at this temperature without intervention. We exist only because the body contains many substances called **enzymes**, which increase the rates of these reactions. In fact, almost every biologically important reaction is assisted by a specific enzyme.

Although it is possible to use higher temperatures to speed up commercially important reactions, such as the Haber process for synthesizing ammonia, this is very expensive. In a chemical plant an increase in temperature means significantly increased costs for energy. The use of an appropriate catalyst allows a reaction to proceed rapidly at a relatively low temperature and can therefore hold down production costs.

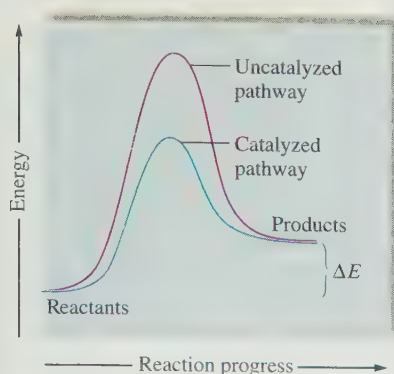


FIGURE 12.15
Energy plots for a catalyzed and an uncatalyzed pathway for a given reaction.

A **catalyst** is a substance that speeds up a reaction without being consumed itself. Just as virtually all vital biologic reactions are assisted by enzymes (biologic catalysts), almost all industrial processes also involve the use of catalysts. For example, the production of sulfuric acid uses vanadium(V) oxide, and the Haber process uses a mixture of iron and iron oxide.

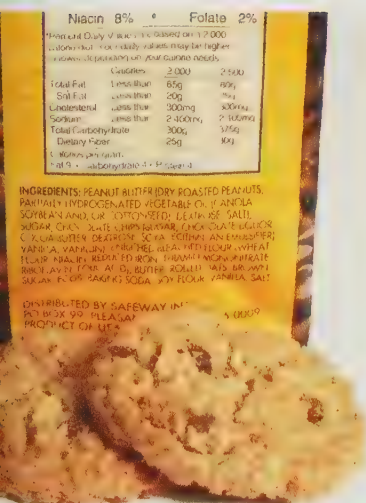
How does a catalyst work? Remember that for each reaction a certain energy barrier must be surmounted. How can we make a reaction occur faster without raising the temperature to increase the molecular energies? The solution is to provide a new pathway for the reaction, one with a *lower activation energy*. This is what a catalyst does, as is shown in Fig. 12.15. Because the catalyst allows the reaction to occur with a lower activation energy, a much larger fraction of collisions is effective at a given temperature, and the reaction rate is increased. This effect is illustrated in Fig. 12.16. Note from this diagram that although a catalyst lowers the activation energy E_a for a reaction, it does not affect the energy difference ΔE between products and reactants.

Catalysts are classified as homogeneous or heterogeneous. A **homogeneous catalyst** is one that is *present in the same phase as the reacting molecules*. A **heterogeneous catalyst** exists *in a different phase*, usually as a solid.

Heterogeneous Catalysis

Heterogeneous catalysis most often involves gaseous reactants being adsorbed on the surface of a solid catalyst. **Adsorption** refers to the collection of one substance on the surface of another substance; *absorption* refers to the penetration of one substance into another. Water is *absorbed* by a sponge.

An important example of heterogeneous catalysis occurs in the hydrogenation of unsaturated hydrocarbons, compounds composed mainly of carbon and hydrogen with some carbon-carbon double bonds. Hydrogenation is an important industrial process used to change unsaturated fats, occurring as oils, to saturated fats (solid shortenings such as Crisco) in which the $C=C$ bonds have been converted to $C-C$ bonds through addition of hydrogen.



These cookies contain partially hydrogenated vegetable oil.

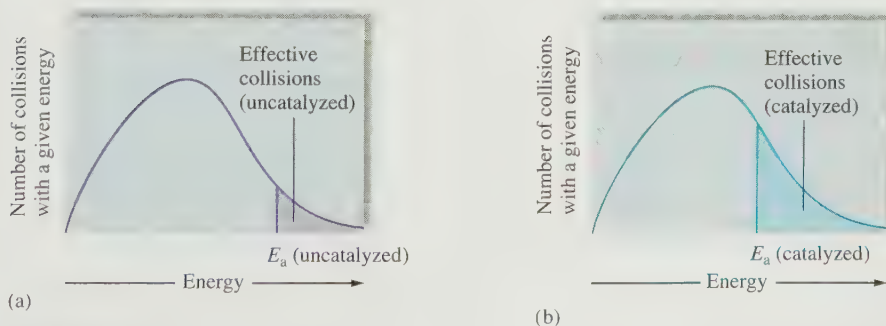
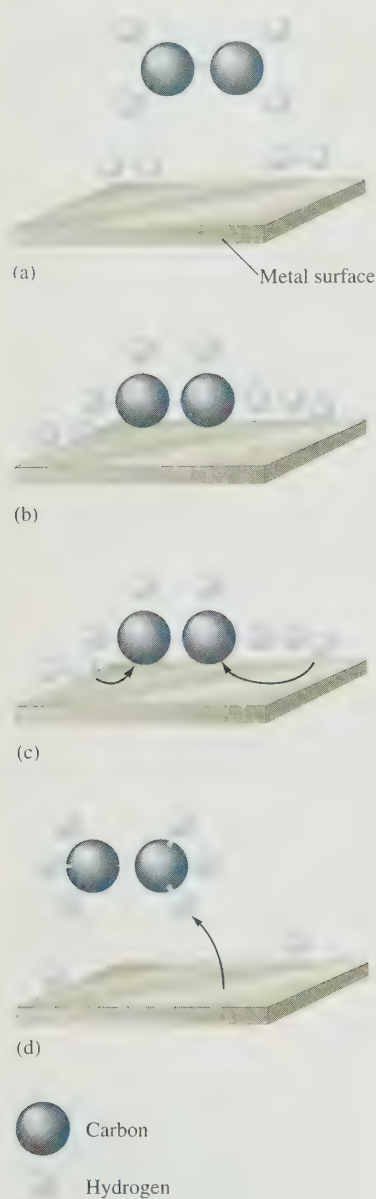


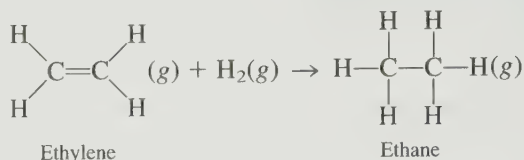
FIGURE 12.16

Effect of a catalyst on the number of reaction-producing collisions. Because a catalyst provides a reaction pathway with a lower activation energy, a much greater fraction of the collisions is effective for the catalyzed pathway (b) than for the uncatalyzed pathway (a) (at a given temperature). This allows reactants to become products at a much higher rate, even though there is no temperature increase.

**FIGURE 12.17**

Heterogeneous catalysis of the hydrogenation of ethylene. (a) The reactants above the metal surface. (b) Hydrogen is adsorbed onto the metal surface, forming metal–hydrogen bonds and breaking the H—H bonds. The π bond in ethylene is broken and metal–carbon bonds are formed during adsorption. (c) The adsorbed molecules and atoms migrate toward each other on the metal surface, forming new C—H bonds. (d) The C atoms in ethane (C₂H₆) have completely saturated bonding capacities and so cannot bind strongly to the metal surfaces. The C₂H₆ molecule thus escapes.

A simple example of hydrogenation involves ethylene:



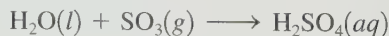
This reaction is quite slow at normal temperatures, mainly because the strong bond in the hydrogen molecule results in a large activation energy for the reaction. However, the reaction rate can be greatly increased by using a solid catalyst of platinum, palladium, or nickel. The hydrogen and ethylene adsorb on the catalyst surface, where the reaction occurs. The main function of the catalyst apparently is to allow formation of metal–hydrogen interactions that weaken the H—H bonds and facilitate the reaction. The mechanism is illustrated in Fig. 12.17.

Typically, heterogeneous catalysis involves four steps:

1. Adsorption and activation of the reactants
2. Migration of the adsorbed reactants on the surface
3. Reaction of the adsorbed substances
4. Escape, or *desorption*, of the products

Heterogeneous catalysis also occurs in the oxidation of gaseous sulfur dioxide to gaseous sulfur trioxide. This process is especially interesting because it illustrates both positive and negative consequences of chemical catalysis.

The negative side is the formation of damaging air pollutants. Recall that sulfur dioxide, a toxic gas with a choking odor, is formed whenever sulfur-containing fuels are burned. However, it is sulfur trioxide that causes most of the environmental damage, mainly through the production of acid rain. When sulfur trioxide combines with a droplet of water, sulfuric acid is formed:



This sulfuric acid can cause considerable damage to vegetation, buildings and statues, and fish populations.

Sulfur dioxide is *not* rapidly oxidized to sulfur trioxide in clean, dry air. Why, then, is there a problem? The answer is catalysis. Dust particles and water droplets catalyze the reaction between SO₂ and O₂ in the air.

On the positive side, the heterogeneous catalysis of the oxidation of SO₂ is used to advantage in the manufacture of sulfuric acid, where the reaction of O₂ and SO₂ to form SO₃ is catalyzed by a solid mixture of platinum and vanadium(V) oxide.

Heterogeneous catalysis is also utilized in the catalytic converters in automobile exhaust systems. The exhaust gases, containing compounds such as nitric

CHEMICAL IMPACT

Automobiles: Air Purifiers?

Outlandish as it may seem, a new scheme has been proposed to turn automobiles into air purifiers, devouring the pollutants ozone and carbon monoxide. Engelhard Corporation, an Iselin, New Jersey, company that specializes in the manufacture of catalytic converters for automotive exhaust systems, has developed a catalyst that decomposes ozone to oxygen and converts carbon monoxide to carbon dioxide. Engelhard proposes to paint the catalyst on auto-

mobile radiators and air-conditioner compressors where fans draw large volumes of air for cooling purposes. The catalyst works well at the warm temperatures present on the surfaces of these devices. The idea is to let cars destroy pollutants using nothing but the catalyst and waste radiator heat.

It's an intriguing idea. The residents of Los Angeles drive nearly 300 million miles every day. At that rate, they could process a lot of air.

oxide, carbon monoxide, and unburned hydrocarbons, are passed through a converter containing beads of solid catalyst (see Fig. 12.18). The catalyst promotes the conversion of carbon monoxide to carbon dioxide, hydrocarbons to carbon dioxide and water, and nitric oxide to nitrogen gas to lessen the environmental impact of the exhaust gases. However, this beneficial catalysis can, unfortunately, be accompanied by the unwanted catalysis of the oxidation of SO_2 to SO_3 , which reacts with the moisture present to form sulfuric acid.

Because of the complex nature of the reactions that take place in the converter, a mixture of catalysts is used. The most effective catalytic materials are transition metal oxides and noble metals such as palladium and platinum.

Homogeneous Catalysis

A homogeneous catalyst exists in the same phase as the reacting molecules. There are many examples in both the gas and liquid phases. One such example is the unusual catalytic behavior of nitric oxide toward ozone. In the troposphere, that part of the atmosphere closest to earth, nitric oxide catalyzes ozone production. However, in the upper atmosphere it catalyzes the decomposition of ozone. Both these effects are unfortunate environmentally.

In the lower atmosphere, NO is produced in any high-temperature combustion process where N_2 is present. The reaction

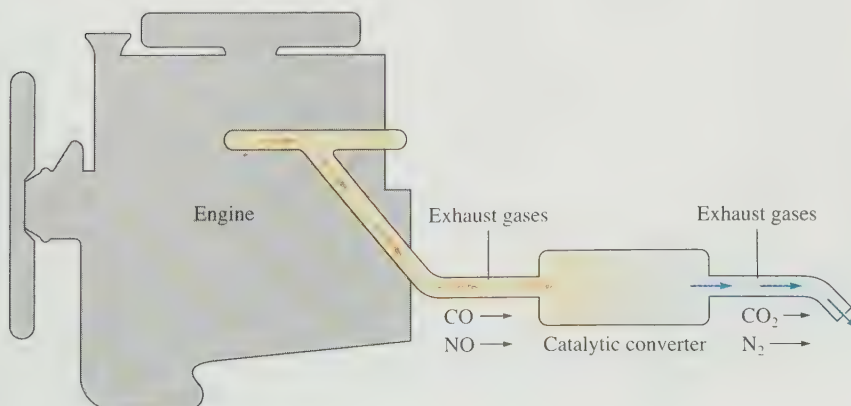
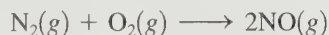


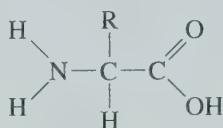
FIGURE 12.18

The exhaust gases from an automobile engine are passed through a catalytic converter to minimize environmental damage.

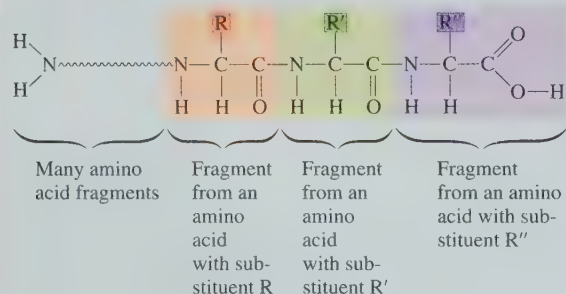
CHEMICAL IMPACT

Enzymes: Nature's Catalysts

The most impressive examples of homogeneous catalysis occur in nature, where the complex reactions necessary for plant and animal life are made possible by enzymes. Enzymes are large molecules specifically tailored to facilitate a given type of reaction. Usually enzymes are proteins, an important class of biomolecules constructed from α -amino acids that have the general structure



where R represents any one of 20 different substituents. These amino acid molecules can be “hooked together” to form a *polymer* (a word meaning “many parts”) called a *protein*. The general structure of a protein can be represented as follows:



Since specific proteins are needed by the human body, the proteins in food must be broken into their constituent amino acids, which are then used to construct new proteins in the body's cells. The reaction in which a protein is broken down one amino acid at a time is shown in Fig. 12.19. Note that in this reaction a water molecule reacts with a protein molecule to produce an amino acid and a new protein containing one less amino acid. Without the enzymes found in human cells, this reaction would be much too slow to be useful. One of these enzymes is *carboxypeptidase-A*, a zinc-containing protein (Fig. 12.20).

Carboxypeptidase-A captures the protein to be acted on (called the *substrate*) in a special groove and positions the substrate so that the end is in the active site, where the catalysis occurs (Fig. 12.21). Note that the Zn^{2+} ion bonds to the oxygen of the $\text{C}=\text{O}$ (carbonyl) group. This polarizes the electron density in the carbonyl group, allowing the neigh-

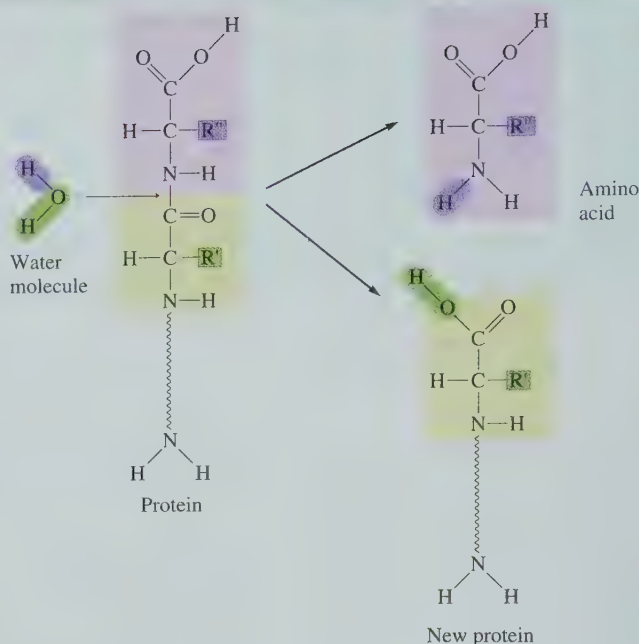


FIGURE 12.19

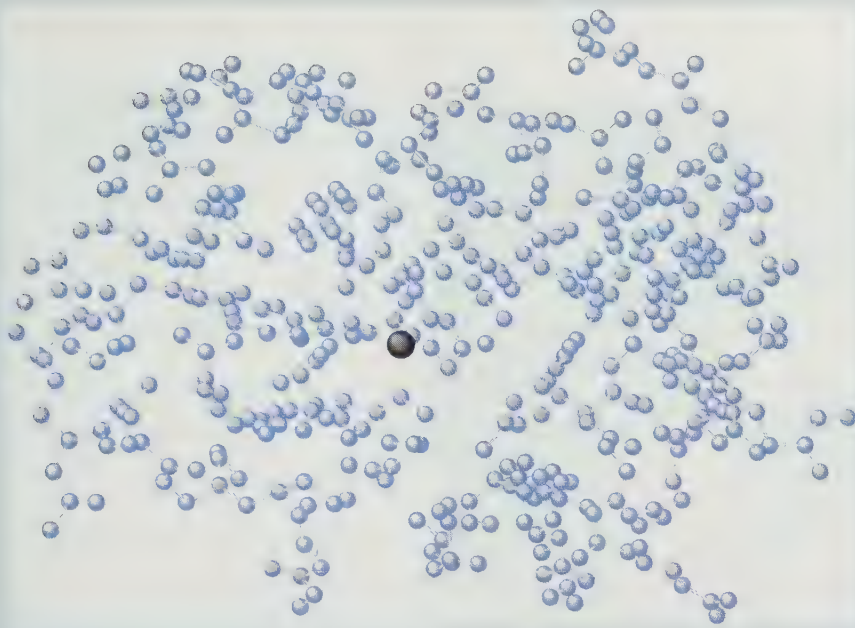
The removal of the end amino acid from a protein by reaction with a molecule of water. The products are an amino acid and a new, smaller protein.

boring C—N bond to be broken much more easily. When the reaction is completed, the remaining portion of the substrate protein and the newly formed amino acid are released by the enzyme.

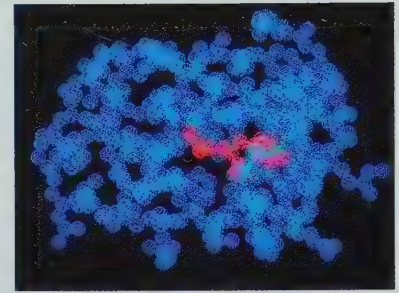
The process just described for carboxypeptidase-A is characteristic of the behavior of other enzymes. Enzyme catalysis can be represented by the series of reactions shown below:



where E represents the enzyme, S represents the substrate, $\text{E} \cdot \text{S}$ represents the enzyme-substrate complex, and P represents the products. The enzyme and substrate form a complex, where the reaction occurs. The enzyme then releases the product and is ready to repeat the process. The most amazing thing about enzymes is their efficiency. Because an enzyme plays its catalytic role over and over and very rapidly, only a tiny amount of enzyme is required. This makes the isolation of enzymes for study quite difficult.



(a)



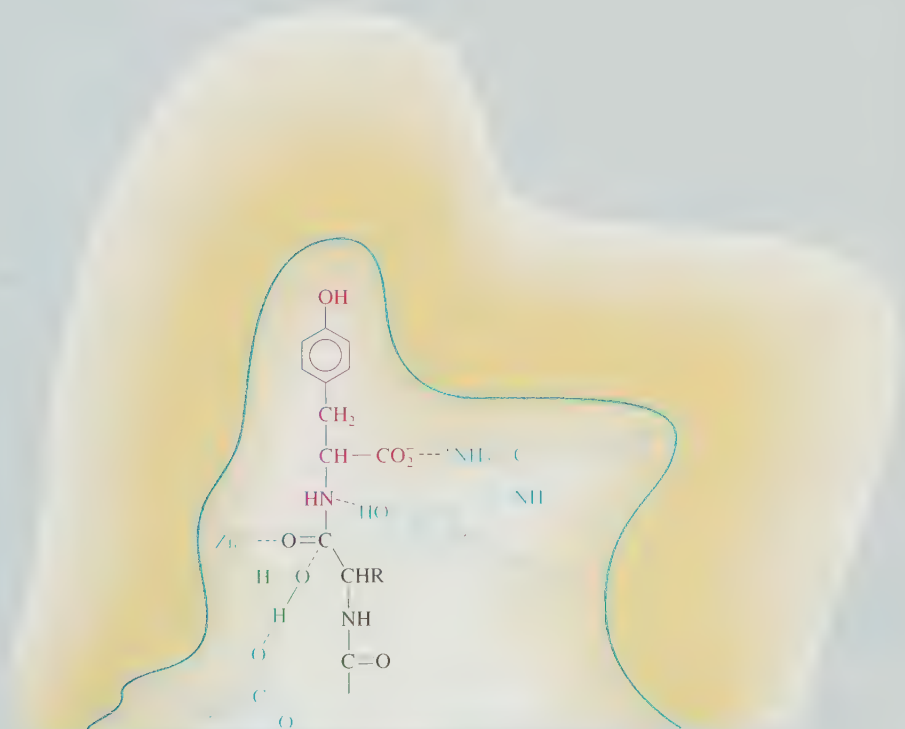
(b)

FIGURE 12.20

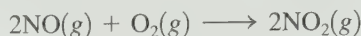
(a) The structure of the enzyme carboxypeptidase-A, which contains 307 amino acids. The zinc ion is shown above as a black sphere in the center. (b) Carboxypeptidase-A with a substrate (pink) in place.

FIGURE 12.21

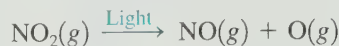
Protein–substrate interaction. The substrate is shown in black and red, with the red representing the terminal amino acid. Blue indicates side chains from the enzyme that help bind the substrate.



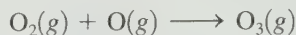
is very slow at normal temperatures because of the very strong $\text{N}\equiv\text{N}$ and $\text{O}=\text{O}$ bonds. However, at elevated temperatures, such as those found in the internal combustion engines of automobiles, significant quantities of NO form. Some of this NO is converted back to N_2 in the catalytic converter, but significant amounts escape into the atmosphere to react with oxygen:



In the atmosphere, NO_2 can absorb light and decompose as follows:



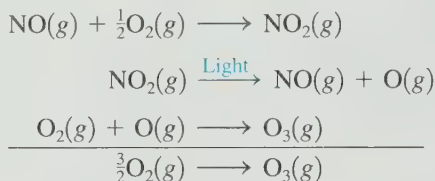
The oxygen atom is very reactive and can combine with oxygen molecules to form ozone:



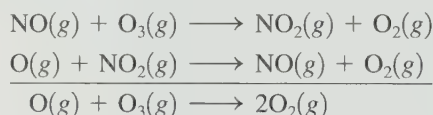
Although O_2 is represented here as the oxidizing agent for NO , the actual oxidizing agent is probably some type of peroxide compound produced by reaction of oxygen with pollutants. The direct reaction of NO and O_2 is very slow.

Ozone is a powerful oxidizing agent that can react with other air pollutants to form substances irritating to the eyes and lungs, and is itself very toxic.

In this series of reactions, nitric oxide is acting as a true catalyst because it assists the production of ozone without being consumed itself. This can be seen by summing the reactions:

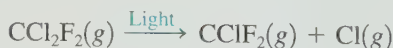


In the upper atmosphere, the presence of nitric oxide has the opposite effect—the depletion of ozone. The series of reactions involved is

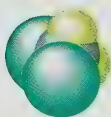
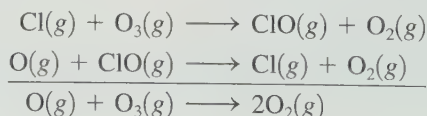


Nitric oxide is again catalytic, but here its effect is to change O_3 to O_2 . This is a potential problem because O_3 , which absorbs ultraviolet light, is necessary to protect us from the harmful effects of this high-energy radiation. That is, we want O_3 in the upper atmosphere to block ultraviolet radiation from the sun but not in the lower atmosphere, where we would have to breathe it and its oxidation products.

The ozone layer is also threatened by *Freons*, a group of stable, noncorrosive compounds, until recently, used as refrigerants and as propellants in aerosol cans. The most commonly used substance of this type was Freon-12 (CCl_2F_2). The chemical inertness of Freons makes them valuable but also creates a problem, since they remain in the environment a long time. Eventually, they migrate into the upper atmosphere to be decomposed by high-energy light. Among the decomposition products are chlorine atoms:



These chlorine atoms can catalyze the decomposition of ozone:

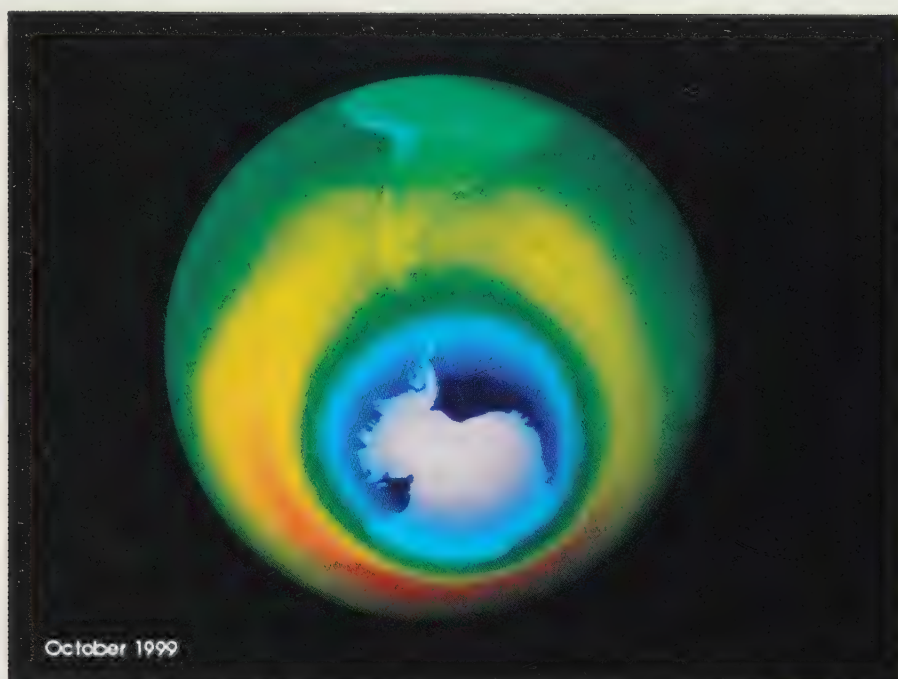


Freon-12.



Ozone.

This graphic shows data from the Total Ozone Mapping Spectrometer (TOMS) Earth Probe.



The problem of Freons has been brought into strong focus by the discovery of a mysterious “hole” in the ozone layer in the stratosphere over Antarctica. Studies performed there to find the reason for the hole have found unusually high levels of chlorine monoxide (ClO). This strongly implicates the Freons in the atmosphere as being responsible for the ozone destruction.

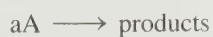
Because they pose environmental problems, Freons have been banned by international agreement. Substitute compounds are now being used.

For Review

Summary

Even though a chemical reaction may have a strong tendency to occur thermodynamically, it is not necessarily fast. Chemical kinetics is the study of the factors that control the rates of chemical reactions. The reaction rate is defined as the change in concentration of a reactant or product per unit of time. Kinetic measurements are usually made under conditions where the reverse reaction is insignificant. Then only the forward reaction is important in determining the rate.

There are two kinds of rate laws: the differential rate law (or just rate law) and the integrated rate law. The rate law for a reaction of the type



describes the dependence of the rate on the concentration of A:

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]^n$$

Key Terms

chemical kinetics

Section 12.1

reaction rate

instantaneous rate

Section 12.2

rate law

rate constant

order

(differential) rate law

integrated rate law

Section 12.3

method of initial rates
initial rate
overall reaction order

Section 12.4

first-order reaction
integrated first-order rate law
half-life of a reactant
integrated second-order rate law
zero-order reaction
integrated zero-order rate law
pseudo-first-order rate law

Section 12.6

reaction mechanism
intermediate
elementary step
molecularity
unimolecular step
bimolecular step
termolecular step
rate-determining step

Section 12.7

collision model
activation energy
activated complex (transition state)
molecular orientations
steric factor
Arrhenius equation
frequency factor

Section 12.8

enzyme
catalyst
homogeneous catalyst
heterogeneous catalyst
adsorption

where k is called the rate constant and n is the order of the reaction in A. The rate is defined as the negative of $\Delta[A]/\Delta t$ because $[A]$ is decreasing (as the reactants are used up in the reaction). The value for n (the order) cannot be determined from the balanced equation for the reaction but must be found experimentally. For a first-order reaction n is 1 and the rate $= k[A]$. For a second-order reaction n is 2 and the rate $= k[A]^2$. For a zero-order reaction n is 0 and the rate $= k$.

A common experimental method for determining the rate law is the method of initial rates in which several runs are carried out with different initial concentrations, and the rate is measured for each at a value of t close to $t = 0$.

An integrated rate law expresses reactant concentrations as a function of time. The integrated rate law for a first-order reaction is

$$\ln[A] = -kt + \ln[A]_0$$

where $[A]_0$ is the initial concentration of A. Thus we can calculate $[A]$ at any time, given $[A]_0$ and k . For a reaction that shows first-order kinetics, a plot of $\ln[A]$ versus time is a straight line.

The half-life ($t_{1/2}$) of a reaction is the time required for a reactant to reach half of its original concentration. For first-order reactions the half-life is independent of concentration:

$$t_{1/2} = \frac{0.693}{k}$$

The integrated rate law for a second-order reaction is

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$$

Consequently, if a plot of $1/[A]$ versus time for a given reaction is a straight line, then the rate must be second order in A. For second-order kinetics, the half-life is dependent on both k and $[A]_0$:

$$t_{1/2} = \frac{1}{k[A]_0}$$

The integrated rate law for a zero-order reaction is

$$[A] = -kt + [A]_0$$

and the half-life is

$$t_{1/2} = \frac{[A]_0}{2k}$$

For a reaction with several reactants, the overall reaction order is the sum of the individual orders. We can determine the orders for this type of reaction by making the concentration of a particular reactant small in comparison to those of the other reactants.

A reaction mechanism is a series of elementary steps by which a given reaction occurs. The rate law for each step can be written from its molecularity, that is, the number of species that must collide to produce the reaction indicated by that step. A unimolecular step is always first order, and a bimolecular step is always second order.

For a mechanism to be acceptable, the sum of the elementary steps must give the overall balanced equation for the reaction, and the mechanism must give a rate

law that agrees with the experimentally determined rate law. Multistep reactions often have one step that is much slower than the others. This is called the rate-determining step, since the overall rate of the reaction is limited by the rate of this step.

Chemical kinetics can be described by the collision model, which assumes that molecules must collide to react. In terms of this model, a certain threshold energy called the activation energy E_a must be overcome for a collision to produce a chemical reaction. E_a is the energy needed to rearrange the bonds in the molecules to form products. Both the rate of a reaction and the effect of temperature on the rate depend on the size of E_a .

Molecular orientation during a collision is also important, since not every collision will have the molecules aligned in an effective way. The factors affecting k can be described by the Arrhenius equation

$$k = Ae^{-E_a/RT}$$

where A is a factor reflecting collision frequency and molecular orientation and $e^{-E_a/RT}$ represents the fraction of collisions with sufficient energy to produce a reaction. The value of E_a can be determined by measuring values of k at two or more temperatures.

A catalyst is a substance that speeds up a reaction without being consumed. A catalyst operates by providing a lower-energy pathway for the reaction in question. Enzymes are biologic catalysts. A homogeneous catalyst is present in the same phase as the reacting molecules, and a heterogeneous catalyst exists in a different phase.

In-Class Discussion Questions*

These questions are designed to be considered by groups of students in class. Often these questions work well for introducing a particular topic in class.

1. Define *stability* from both a kinetic and thermodynamic perspective. Give examples to show the differences in these concepts.
2. Describe at least two experiments you could perform to determine a rate law.
3. Make a graph of $[A]$ versus time for zero-, first-, and second-order reactions. From these graphs, compare successive half-lives.
4. How does temperature affect k , the rate constant? Explain.
5. Consider the following statements: "In general, the rate of a chemical reaction increases a bit at first because it takes a while for the reaction to get 'warmed up.' After that, however, the rate of the reaction decreases because its rate is dependent on the concentrations of the reactants, and these are decreasing." Indicate everything that is correct in these statements, and indicate everything that is incorrect. Correct the incorrect statements and explain.
6. For the reaction $A + B \rightarrow C$, explain at least two ways in which the rate law could be zero order in chemical A.

7. A friend of yours states, "A balanced equation tells us how chemicals interact. Therefore, we can determine the rate law directly from the balanced equation." What do you tell your friend?
8. Provide a conceptual rationale for the differences in the half-lives of zero-, first-, and second-order reactions.

A blue question or exercise number indicates that the answer to that question or exercise appears at the back of this book and a solution appears in the *Solutions Guide*.

Questions

9. Distinguish among the initial rate, average rate, and instantaneous rate of a chemical reaction. Which of these rates usually has the largest value?
10. Define each of the following.
 - a. elementary step
 - b. reaction mechanism
 - c. rate-determining step
11. Why is the rate of a reaction affected by each of the following?
 - a. frequency of collisions
 - b. kinetic energy of collisions
 - c. orientation of collisions
12. Define what is meant by unimolecular and bimolecular steps. Why are termolecular steps infrequently seen in chemical reactions?

* In the Questions and the Exercises, the term *rate law* always refers to the differential rate law.

13. Why does a catalyst increase the rate of a reaction? What is the difference between a homogeneous and heterogeneous catalyst? Would a given reaction necessarily have the same rate law for both a catalyzed and an uncatalyzed pathway? Explain.
14. Hydrogen reacts explosively with oxygen. However, a mixture of H_2 and O_2 can exist indefinitely at room temperature. Explain why H_2 and O_2 do not react under these conditions.
15. Each of the statements given below is false. Explain why.
- The activation energy of a reaction depends on the overall energy change (ΔE) for the reaction.
 - The rate law for a reaction can be deduced from examination of the overall balanced equation for the reaction.
 - Most reactions occur by one-step mechanisms.
16. For the reaction



the observed rate law is

$$\text{Rate} = k[\text{NO}]^2[\text{H}_2]$$

Which of the changes listed below would affect the value of the rate constant k ?

- increasing the partial pressure of hydrogen gas
- changing the temperature
- using an appropriate catalyst

Exercises

In this section similar exercises are paired.

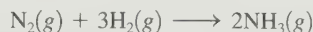
Reaction Rates

17. Consider the reaction



If, in a certain experiment, over a specific time period, 0.0048 mol PH_3 is consumed in a 2.0-L container each second of reaction, what are the rates of production of P_4 and H_2 in this experiment?

18. In the Haber process for the production of ammonia,



what is the relationship between the rate of production of ammonia and the rate of consumption of hydrogen?

19. What are the units for each of the following if the concentrations are expressed in moles per liter and the time in seconds?
- rate of a chemical reaction
 - rate constant for a zero-order rate law
 - rate constant for a first-order rate law
 - rate constant for a second-order rate law
 - rate constant for a third-order rate law

20. The rate law for the reaction

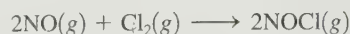


is
$$\text{Rate} = k[\text{Cl}_2]^{1/2}[\text{CHCl}_3]$$

What are the units for k , assuming time in seconds and concentration in mol/L?

Rate Laws from Experimental Data: Initial Rates Method

21. The reaction



was studied at -10°C . The following results were obtained where

$$\text{Rate} = -\frac{\Delta[\text{Cl}_2]}{\Delta t}$$

$[\text{NO}]_0$ (mol/L)	$[\text{Cl}_2]_0$ (mol/L)	Initial Rate (mol/L · min)
0.10	0.10	0.18
0.10	0.20	0.36
0.20	0.20	1.45

- What is the rate law?
- What is the value of the rate constant?

22. The reaction



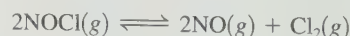
was studied at 25°C . The following results were obtained where

$$\text{Rate} = -\frac{\Delta[\text{S}_2\text{O}_8^{2-}]}{\Delta t}$$

$[\text{I}^-]_0$ (mol/L)	$[\text{S}_2\text{O}_8^{2-}]_0$ (mol/L)	Initial Rate (mol/L · s)
0.080	0.040	12.5×10^{-6}
0.040	0.040	6.25×10^{-6}
0.080	0.020	6.25×10^{-6}
0.032	0.040	5.00×10^{-6}
0.060	0.030	7.00×10^{-6}

- Determine the rate law.
- Calculate a value for the rate constant for each experiment and an average value for the rate constant.

23. The decomposition of nitrosyl chloride was studied:



The following data were obtained where

$$\text{Rate} = -\frac{\Delta[\text{NOCl}]}{\Delta t}$$

$[\text{NOCl}]_0$ (molecules/cm ³)	Initial Rate (molecules/cm ³ · s)
3.0×10^{16}	5.98×10^4
2.0×10^{16}	2.66×10^4
1.0×10^{16}	6.64×10^3
4.0×10^{16}	1.06×10^5

- a. What is the rate law?
 b. Calculate the rate constant.
 c. Calculate the rate constant for the concentrations given in moles per liter.
24. The following data were obtained for the gas-phase decomposition of dinitrogen pentoxide,



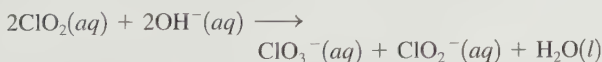
$[\text{N}_2\text{O}_5]_0$ (mol/L)	Initial Rate (mol/L · s)
0.0750	8.90×10^{-4}
0.190	2.26×10^{-3}
0.275	3.26×10^{-3}
0.410	4.85×10^{-3}

Defining the rate as $-\Delta[\text{N}_2\text{O}_5]/\Delta t$, write the rate law and calculate the value of the rate constant.

25. The rate of the reaction between hemoglobin (Hb) and carbon monoxide (CO) was studied at 20°C. The following data were collected with all concentration units in $\mu\text{mol/L}$. (A hemoglobin concentration of $2.21 \mu\text{mol/L}$ is equal to $2.21 \times 10^{-6} \text{ mol/L}$.)

$[\text{Hb}]_0$ ($\mu\text{mol/L}$)	$[\text{CO}]_0$ ($\mu\text{mol/L}$)	Initial Rate ($\mu\text{mol/L} \cdot \text{s}$)
2.21	1.00	0.619
4.42	1.00	1.24
4.42	3.00	3.71

- a. Determine the orders of this reaction with respect to Hb and CO.
 b. Determine the rate law.
 c. Calculate the value of the rate constant.
 d. What would be the initial rate for an experiment with $[\text{Hb}]_0 = 3.36 \mu\text{mol/L}$ and $[\text{CO}]_0 = 2.40 \mu\text{mol/L}$?
26. The following data were obtained for the reaction



where
$$\text{Rate} = -\frac{\Delta[\text{ClO}_2]}{\Delta t}$$

$[\text{ClO}_2]_0$ (mol/L)	$[\text{OH}^-]_0$ (mol/L)	Initial Rate (mol/L · s)
0.0500	0.100	5.75×10^{-2}
0.100	0.100	2.30×10^{-1}
0.100	0.0500	1.15×10^{-1}

- a. Determine the rate law and the value of the rate constant.
 b. What would be the initial rate for an experiment with $[\text{ClO}_2]_0 = 0.175 \text{ mol/L}$ and $[\text{OH}^-]_0 = 0.0844 \text{ mol/L}$?

Integrated Rate Laws

27. The decomposition of hydrogen peroxide was studied, and the following data were obtained at a particular temperature:

Time (s)	$[\text{H}_2\text{O}_2]$ (mol/L)
0	1.00
120 ± 1	0.91
300 ± 1	0.78
600 ± 1	0.59
1200 ± 1	0.37
1800 ± 1	0.22
2400 ± 1	0.13
3000 ± 1	0.082
3600 ± 1	0.050

Assuming that

$$\text{Rate} = -\frac{\Delta[\text{H}_2\text{O}_2]}{\Delta t}$$

determine the rate law, the integrated rate law, and the value of the rate constant. Calculate $[\text{H}_2\text{O}_2]$ at 4000. s after the start of the reaction.

28. A certain reaction has the following general form:



At a particular temperature and $[\text{A}]_0 = 2.00 \times 10^{-2} \text{ M}$, concentration versus time data were collected for this reaction, and a plot of $\ln[\text{A}]$ versus time resulted in a straight line with a slope value of $-2.97 \times 10^{-2} \text{ min}^{-1}$.

- a. Determine the rate law, the integrated rate law, and the value of the rate constant for this reaction.
 b. Calculate the half-life for this reaction.
 c. How much time is required for the concentration of A to decrease to $2.50 \times 10^{-3} \text{ M}$?

29. The rate of the reaction



depends only on the concentration of nitrogen dioxide below 225°C. At a temperature below 225°C, the following data were collected:

Time (s)	[NO ₂] (mol/L)
0	0.500
1.20×10^3	0.444
3.00×10^3	0.381
4.50×10^3	0.340
9.00×10^3	0.250
1.80×10^4	0.174

Determine the rate law, the integrated law, and the value of the rate constant. Calculate [NO₂] at 2.70×10^4 s after the start of the reaction.

30. A certain reaction has the following general form:



At a particular temperature and $[A]_0 = 2.80 \times 10^{-3}$ M, concentration versus time data were collected for this reaction, and a plot of $1/[A]$ versus time resulted in a straight line with a slope value of $+3.60 \times 10^{-2}$ L/mol $\cdot$ s.

- Determine the rate law, the integrated rate law, and the value of the rate constant for this reaction.
- Calculate the half-life for this reaction.
- How much time is required for the concentration of A to decrease to 7.00×10^{-4} M?

31. The decomposition of ethanol (C₂H₅OH) on an alumina (Al₂O₃) surface



was studied at 600 K. Concentration versus time data were collected for this reaction, and a plot of $[A]$ versus time resulted in a straight line with a slope of -4.00×10^{-5} mol/L $\cdot$ s.

- Determine the rate law, the integrated rate law, and the value of the rate constant for this reaction.
 - If the initial concentration of C₂H₅OH was 1.25×10^{-2} M, calculate the half-life for this reaction.
 - How much time is required for all the 1.25×10^{-2} M C₂H₅OH to decompose?
32. At 500 K in the presence of a copper surface, ethanol decomposes according to the equation



The pressure of C₂H₅OH was measured as a function of time and the following data were obtained:

Time (s)	$P_{C_2H_5OH}$ (torr)
0	250.
100.	237
200.	224
300.	211
400.	198
500.	185

Since the pressure of a gas is directly proportional to the concentration of gas, we can express the rate law for a gaseous reaction in terms of partial pressures. Using the above data, deduce the rate law, the integrated rate law, and the value of the rate constant, all in terms of pressure units in atm and time in seconds. Predict the pressure of C₂H₅OH after 900. s from the start of the reaction. (*Hint:* To determine the order of the reaction with respect to C₂H₅OH, compare how the pressure of C₂H₅OH decreases with each time listing.)

33. The dimerization of butadiene



was studied at 500. K, and the following data were obtained:

Time (s)	[C ₄ H ₆] (mol/L)
195	1.6×10^{-2}
604	1.5×10^{-2}
1246	1.3×10^{-2}
2180	1.1×10^{-2}
6210	0.68×10^{-2}

Assuming that

$$\text{Rate} = -\frac{\Delta[C_4H_6]}{\Delta t}$$

determine the form of the rate law, the integrated rate law, and the rate constant for this reaction. (These are actual experimental data, so they may not give a perfectly straight line.)

34. The rate of the reaction



was studied at a certain temperature.

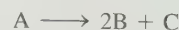
- In the first set of experiments, NO₂ was in large excess, at a concentration of 1.0×10^{13} molecules/cm³ with the following data collected:

Time (s)	[O] (atoms/cm ³)
0	5.0×10^9
1.0×10^{-2}	1.9×10^9
2.0×10^{-2}	6.8×10^8
3.0×10^{-2}	2.5×10^8

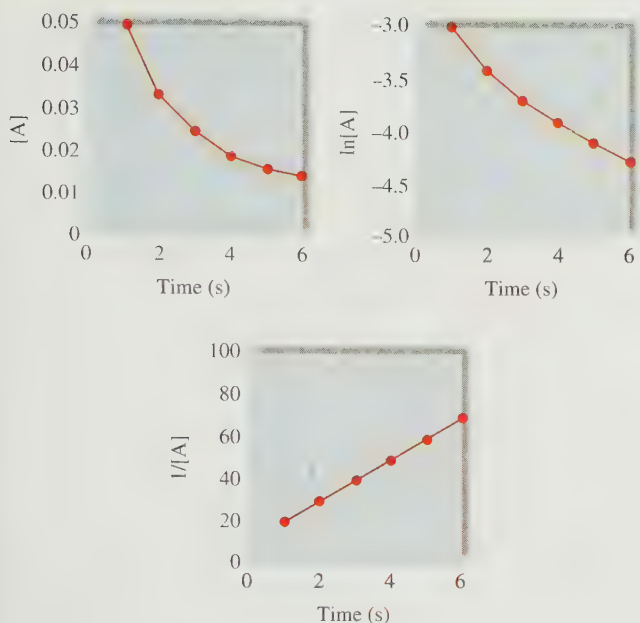
What is the order of the reaction with respect to oxygen atoms?

- The reaction is known to be first order with respect to NO₂. Determine the overall rate law and the value of the rate constant.

35. Experimental data for the reaction



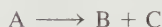
have been plotted in the following three different ways (with concentration units in mol/L):



What is the order of the reaction with respect to A and what is the initial concentration of A?

36. Consider the data plotted in Exercise 35 when answering the following questions.
- What is the concentration of A after 9 s?
 - What are the first three half-lives for this experiment?

37. The reaction



is known to be zero order in A and to have a rate constant of $5.0 \times 10^{-2} \text{ mol/L} \cdot \text{s}$ at 25°C . An experiment was run at 25°C where $[A]_0 = 1.0 \times 10^{-3} \text{ M}$.

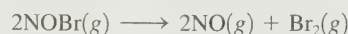
- Write the integrated rate law for this reaction.
 - Calculate the half-life for the reaction.
 - Calculate the concentration of B after $5.0 \times 10^{-3} \text{ s}$ has elapsed.
38. The radioactive isotope ^{32}P decays by first-order kinetics and has a half-life of 14.3 days. How long does it take for 95.0% of a sample of ^{32}P to decay?
39. A first-order reaction is 38.5% complete in 480. s.
- Calculate the rate constant.
 - What is the value of the half-life?
 - How long will it take for the reaction to go to 25%, 75%, and 95% completion?
40. The rate law for the decomposition of phosphine (PH_3) is

$$\text{Rate} = -\frac{\Delta[\text{PH}_3]}{\Delta t} = k[\text{PH}_3]$$

It takes 120. s for 1.00 M PH_3 to decrease to 0.250 M. How much time is required for 2.00 M PH_3 to decrease to a concentration of 0.350 M?

41. It took 143 s for 50.0% of a particular substance to decompose. If the initial concentration was 0.060 M and the decomposition reaction follows second-order kinetics, what is the value of the rate constant?

42. The rate law for the reaction

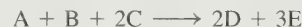


at some temperature is

$$\text{Rate} = -\frac{\Delta[\text{NOBr}]}{\Delta t} = k[\text{NOBr}]^2$$

- If the half-life for this reaction is 2.00 s when $[\text{NOBr}]_0 = 0.900 \text{ M}$, calculate the value of k for this reaction.
 - How much time is required for the concentration of NOBr to decrease to 0.100 M?
43. For the reaction $A \longrightarrow \text{products}$, successive half-lives are observed to be 10.0, 20.0, and 40.0 min for an experiment in which $[A]_0 = 0.10 \text{ M}$. Calculate the concentration of A at the following times.
- 80.0 min
 - 30.0 min

44. Consider the hypothetical reaction



where the rate law is

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A][B]^2$$

An experiment is carried out where $[A]_0 = 1.0 \times 10^{-2} \text{ M}$, $[B]_0 = 3.0 \text{ M}$, and $[C]_0 = 2.0 \text{ M}$. The reaction is started, and after 8.0 seconds, the concentration of A is $3.8 \times 10^{-3} \text{ M}$.

- Calculate k for this reaction.
- Calculate the half-life for this experiment.
- Calculate the concentration of A after 13.0 seconds.
- Calculate the concentration of C after 13.0 seconds.

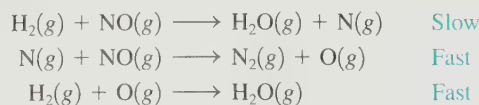
Reaction Mechanisms

45. Write the rate laws for the following elementary reactions.
- $\text{CH}_3\text{NC}(g) \longrightarrow \text{CH}_3\text{CN}(g)$
 - $\text{O}_3(g) + \text{NO}(g) \longrightarrow \text{O}_2(g) + \text{NO}_2(g)$
 - $\text{O}_3(g) \longrightarrow \text{O}_2(g) + \text{O}(g)$
 - $\text{O}_3(g) + \text{O}(g) \longrightarrow 2\text{O}_2(g)$
46. The mechanisms shown below have been proposed to explain the kinetics of the reaction considered in Question 16. Which of the following are acceptable mechanisms? Explain.

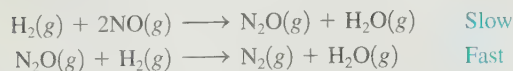
Mechanism I:



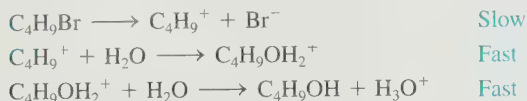
Mechanism II:



Mechanism III:

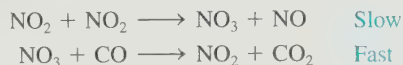


47. A proposed mechanism for a reaction is



Write the rate law expected for this mechanism. What is the overall balanced equation for the reaction? What are the intermediates in the proposed mechanism?

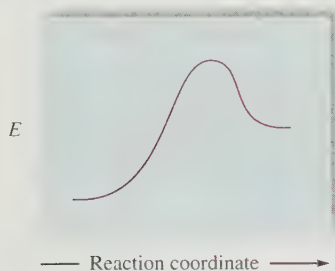
48. The mechanism for the reaction of nitrogen dioxide with carbon monoxide to form nitric oxide and carbon dioxide is thought to be



Write the rate law expected for this mechanism. What is the overall balanced equation for the reaction?

Temperature Dependence of Rate Constants and the Collision Model

49. For the following reaction profile, indicate
- the positions of reactants and products.
 - the activation energy.
 - ΔE for the reaction.



50. Draw a rough sketch of the energy profile for each of the following cases:
- $\Delta E = +10 \text{ kJ/mol}$, $E_a = 25 \text{ kJ/mol}$
 - $\Delta E = -10 \text{ kJ/mol}$, $E_a = 50 \text{ kJ/mol}$
 - $\Delta E = -50 \text{ kJ/mol}$, $E_a = 50 \text{ kJ/mol}$

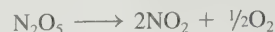
51. The activation energy for the reaction



is 125 kJ/mol , and ΔE for the reaction is -216 kJ/mol . What is the activation energy for the reverse reaction $[\text{NO}(\text{g}) + \text{CO}_2(\text{g}) \longrightarrow \text{NO}_2(\text{g}) + \text{CO}(\text{g})]$?

52. For a certain process, the activation energy is greater for the forward reaction than for the reverse reaction. Does this reaction have a positive or negative value for ΔE ?

53. The rate constant for the gas-phase decomposition of N_2O_5 ,



has the following temperature dependence:

$T(\text{K})$	$k(\text{s}^{-1})$
338	4.9×10^{-3}
318	5.0×10^{-4}
298	3.5×10^{-5}

Make the appropriate graph using these data, and determine the activation energy for this reaction.

54. The reaction



in a certain solvent is first order with respect to $(\text{CH}_3)_3\text{CBr}$ and zero order with respect to OH^- . In several experiments, the rate constant k was determined at different temperatures. A plot of $\ln(k)$ versus $1/T$ was constructed resulting in a straight line with a slope value of $-1.10 \times 10^4 \text{ K}$ and y -intercept of 33.5 . Assume k has units of s^{-1} .

- Determine the activation energy for this reaction.
- Determine the value of the frequency factor A .
- Calculate the value of k at 25°C .

55. At 25°C the first-order rate constant for a reaction is $2.0 \times 10^3 \text{ s}^{-1}$. The activation energy is 15.0 kJ/mol . What is the value of the rate constant at 75°C ?

56. A first-order reaction has rate constants of $4.6 \times 10^{-2} \text{ s}^{-1}$ and $8.1 \times 10^{-2} \text{ s}^{-1}$ at 0°C and 20°C , respectively. What is the value of the activation energy?

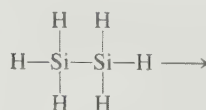
57. A certain reaction has an activation energy of 54.0 kJ/mol . As the temperature is increased from 22°C to a higher temperature, the rate constant increases by a factor of 7.00 . Calculate the higher temperature.

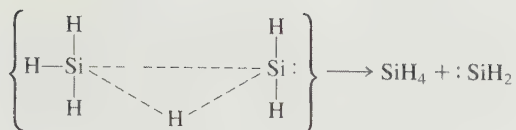
58. Chemists commonly use a rule of thumb that an increase of 10 K in temperature doubles the rate of a reaction. What must the activation energy be for this statement to be true for a temperature increase from 25 to 35°C ?

59. Which of the following reactions would you expect to proceed at a faster rate at room temperature? Why? (Hint: Think of which reaction would have the lower activation energy.)



60. One reason suggested for the instability of long chains of silicon atoms is that the decomposition involves the transition state shown below:

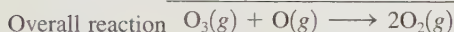
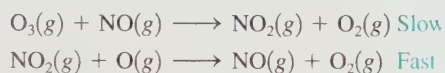




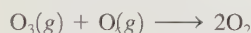
The activation energy for such a process is 210 kJ/mol, which is less than either the Si—Si or the Si—H bond energy. Why would a similar mechanism not be expected to play a very important role in the decomposition of long chains of carbon atoms as seen in organic compounds?

Catalysts

61. One mechanism for the destruction of ozone in the upper atmosphere is

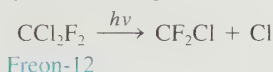


- Which species is a catalyst?
- Which species is an intermediate?
- E_a for the uncatalyzed reaction

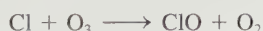


is 14.0 kJ. E_a for the same reaction when catalyzed is 11.9 kJ. What is the ratio of the rate constant for the catalyzed reaction to that for the uncatalyzed reaction at 25°C? Assume that the frequency factor A is the same for each reaction.

62. One of the concerns about the use of Freons is that they will migrate to the upper atmosphere, where chlorine atoms can be generated by the following reaction:



Chlorine atoms can act as a catalyst for the destruction of ozone. The activation energy for the reaction



is 2.1 kJ/mol. Which is the more effective catalyst for the destruction of ozone, Cl or NO? (See Exercise 61.)

63. Assuming that the mechanism for the hydrogenation of C_2H_4 given in Section 12.8 is correct, would you predict that the product of the reaction of C_2H_4 with D_2 would be $\text{CH}_2\text{D}-\text{CH}_2\text{D}$ or CHD_2-CH_3 ? How could the reaction of C_2H_4 with D_2 be used to confirm the mechanism for the hydrogenation of C_2H_4 given in Section 12.8?

64. The decomposition of NH_3 to N_2 and H_2 was studied on two surfaces:

Surface	E_a (kJ/mol)
W	163
Os	197

Without a catalyst, the activation energy is 335 kJ/mol.

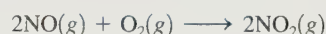
- Which surface is the better heterogeneous catalyst for the decomposition of NH_3 ? Why?
- How many times faster is the reaction at 298 K on the W surface compared with the reaction with no catalyst present? Assume that the frequency factor A is the same for each reaction.
- The decomposition reaction on the two surfaces obeys a rate law of the form

$$\text{Rate} = k \frac{[\text{NH}_3]}{[\text{H}_2]}$$

How can you explain the inverse dependence of the rate on the H_2 concentration?

Additional Exercises

65. The reaction



was studied, and the following data were obtained where

$$\text{Rate} = -\frac{\Delta[\text{O}_2]}{\Delta t}$$

$[\text{NO}]_0$ (molecules/cm ³)	$[\text{O}_2]_0$ (molecules/cm ³)	Initial Rate (molecules/cm ³ · s)
1.00×10^{18}	1.00×10^{18}	2.00×10^{16}
3.00×10^{18}	1.00×10^{18}	1.80×10^{17}
2.50×10^{18}	2.50×10^{18}	3.13×10^{17}

What would be the initial rate for an experiment where $[\text{NO}]_0 = 6.21 \times 10^{18}$ molecules/cm³ and $[\text{O}_2]_0 = 7.36 \times 10^{18}$ molecules/cm³?

66. Sulfuryl chloride (SO_2Cl_2) decomposes to sulfur dioxide (SO_2) and chlorine (Cl_2) by reaction in the gas phase. The following pressure data were obtained when a sample containing 5.00×10^{-2} mol sulfuryl chloride was heated to 600. K in a 5.00×10^{-1} L container.

Time (hours):	0.00	1.00	2.00	4.00	8.00	16.00
$P_{\text{SO}_2\text{Cl}_2}$ (atm):	4.93	4.26	3.52	2.53	1.30	0.34

Defining the rate as $-\frac{\Delta[\text{SO}_2\text{Cl}_2]}{\Delta t}$,

- determine the value of the rate constant for the decomposition of sulfuryl chloride at 600. K.
- what is the half-life of the reaction?
- what fraction of the sulfuryl chloride remains after 20.0 h?

67. For the reaction



the following data were collected, where

$$\text{Rate} = -\frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t}$$

Time (s)	$T = 338 \text{ K}$ $[\text{N}_2\text{O}_5]$	$T = 318 \text{ K}$ $[\text{N}_2\text{O}_5]$
0	$1.00 \times 10^{-1} \text{ M}$	$1.00 \times 10^{-1} \text{ M}$
100.	$6.14 \times 10^{-2} \text{ M}$	$9.54 \times 10^{-2} \text{ M}$
300.	$2.33 \times 10^{-2} \text{ M}$	$8.63 \times 10^{-2} \text{ M}$
600.	$5.41 \times 10^{-3} \text{ M}$	$7.43 \times 10^{-2} \text{ M}$
900.	$1.26 \times 10^{-3} \text{ M}$	$6.39 \times 10^{-2} \text{ M}$

Calculate E_a for this reaction.

68. Experimental values for the temperature dependence of the rate constant for the gas-phase reaction



are as follows:

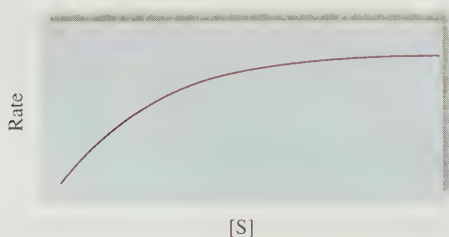
$T \text{ (K)}$	$k \text{ (L/mol} \cdot \text{s)}$
195	1.08×10^9
230.	2.95×10^9
260.	5.42×10^9
298	12.0×10^9
369	35.5×10^9

Make the appropriate graph using these data, and determine the activation energy for this reaction.

69. For enzyme-catalyzed reactions that follow the mechanism



a graph of the rate as a function of $[\text{S}]$, the concentration of the substrate, has the following appearance:



Note that at higher substrate concentrations the rate no longer changes with $[\text{S}]$. Suggest a reason for this.

70. The activation energy of a certain uncatalyzed biochemical reaction is 50.0 kJ/mol. In the presence of a catalyst at 37°C, the rate constant for the reaction increases by a factor of
- 2.50×10^3
- as compared with the uncatalyzed reaction. Assuming the frequency factor
- A
- is the same for both the catalyzed and uncatalyzed reactions, calculate the activation energy for the catalyzed reaction.

Challenge Problems

71. A study was made of the effect of the hydroxide concentration on the rate of the reaction

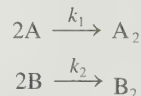


The following data were obtained:

$[\text{I}^-]_0$ (mol/L)	$[\text{OCI}^-]_0$ (mol/L)	$[\text{OH}^-]_0$ (mol/L)	Initial Rate (mol/L · s)
0.0013	0.012	0.10	9.4×10^{-3}
0.0026	0.012	0.10	18.7×10^{-3}
0.0013	0.0060	0.10	4.7×10^{-3}
0.0013	0.018	0.10	14.0×10^{-3}
0.0013	0.012	0.050	18.7×10^{-3}
0.0013	0.012	0.20	4.7×10^{-3}
0.0013	0.018	0.20	7.0×10^{-3}

Determine the rate law and the value of the rate constant for this reaction.

72. Two isomers (A and B) of a given compound dimerize as follows:



Both processes are known to be second order in reactant, and k_1 is known to be 0.250 L/mol · s at 25°C. In a particular experiment A and B were placed in separate containers at 25°C, where $[\text{A}]_0 = 1.00 \times 10^{-2} \text{ M}$ and $[\text{B}]_0 = 2.50 \times 10^{-2} \text{ M}$. It was found that after each reaction had progressed for 3.00 min, $[\text{A}] = 3.00[\text{B}]$. In this case the rate laws are defined as

$$\text{Rate} = -\frac{\Delta[\text{A}]}{\Delta t} = k_1[\text{A}]^2$$

$$\text{Rate} = -\frac{\Delta[\text{B}]}{\Delta t} = k_2[\text{B}]^2$$

- Calculate the concentration of A_2 after 3.00 min.
 - Calculate the value of k_2 .
 - Calculate the half-life for the experiment involving A.
73. The reaction



was studied by performing two experiments. In the first experiment the rate of disappearance of NO was followed in the presence of a large excess of O₃. The results were as follows ([O₃] remains effectively constant at 1.0×10^{14} molecules/cm³):

Time (ms)	[NO] (molecules/cm ³)
0	6.0×10^8
100 ± 1	5.0×10^8
500 ± 1	2.4×10^8
700 ± 1	1.7×10^8
1000 ± 1	9.9×10^7

In the second experiment [NO] was held constant at 2.0×10^{14} molecules/cm³. The data for the disappearance of O₃ are as follows:

Time (ms)	[O ₃] (molecules/cm ³)
0	1.0×10^{10}
50 ± 1	8.4×10^9
100 ± 1	7.0×10^9
200 ± 1	4.9×10^9
300 ± 1	3.4×10^9

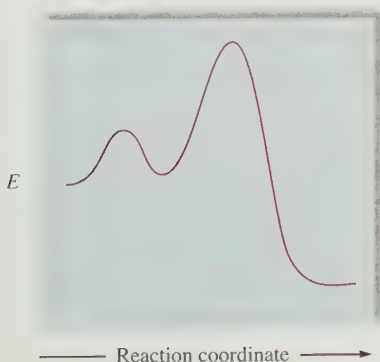
- What is the order with respect to each reactant?
- What is the overall rate law?
- What is the value of the rate constant from each set of experiments?

$$\text{Rate} = k'[\text{NO}]^x \quad \text{Rate} = k''[\text{O}_3]^y$$

- What is the value of the rate constant for the overall rate law?

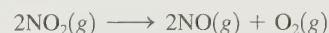
$$\text{Rate} = k[\text{NO}]^x[\text{O}_3]^y$$

74. Most reactions occur by a series of steps. The energy profile for a certain reaction that proceeds by a two-step mechanism is



On the energy profile, indicate

- The positions of reactants and products.
 - The activation energy for the overall reaction.
 - ΔE for the reaction.
 - Which point on the plot represents the energy of the intermediate in the two-step reaction?
 - Which step in the mechanism for this reaction is rate determining, the first or the second step? Explain.
75. Experiments during a recent summer on a number of fireflies (small beetles, *Lampyridae photinus*) showed that the average interval between flashes of individual insects was 16.3 s at 21.0°C and 13.0 s at 27.8°C.
- What is the apparent activation energy of the reaction that controls the flashing?
 - What would be the average interval between flashes of an individual firefly at 30.0°C?
 - Compare the observed intervals and the one you calculated in part (b) to the rule of thumb that the Celsius temperature is 54 minus twice the interval between flashes.
76. The decomposition of NO₂(g) occurs by the following bimolecular elementary reaction:



The rate constant at 273 K is 2.3×10^{-12} L/mol · s, and the activation energy is 111 kJ/mol. How long will it take for the concentration of NO₂(g) to decrease from an initial partial pressure of 2.5 atm to 1.5 atm at 500. K? Assume ideal gas behavior.

Marathon Problem

This problem is designed to incorporate several concepts and techniques into one situation. Marathon Problems can be used in class by groups of students to help facilitate problem-solving skills.

77. Consider the following reaction:



At 25°C, the following two experiments were run, yielding the following data:

Experiment 1: [Y]₀ = 3.0 M

[CH ₃ X]	Time (h)
$7.08 \times 10^{-3} \text{ M}$	1.0
$4.52 \times 10^{-3} \text{ M}$	1.5
$2.23 \times 10^{-3} \text{ M}$	2.3
$4.76 \times 10^{-4} \text{ M}$	4.0
$8.44 \times 10^{-5} \text{ M}$	5.7
$2.75 \times 10^{-5} \text{ M}$	7.0

Experiment 2: $[Y]_0 = 4.5 M$

$[CH_3X]$	Time (h)
$4.50 \times 10^{-3} M$	0
$1.70 \times 10^{-3} M$	1.0
$4.19 \times 10^{-4} M$	2.5
$1.11 \times 10^{-4} M$	4.0
$2.81 \times 10^{-5} M$	5.5

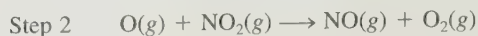
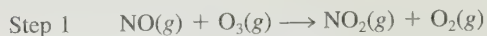
Experiments also were run at 85°C. The value of the rate constant at 85°C was found to be 7.88×10^8 (with the time in units of hours), where $[CH_3X]_0 = 1.0 \times 10^{-2} M$ and $[Y]_0 = 3.0 M$.

- Determine the rate law and the value of k for this reaction at 25°C.
- Determine the half-life at 85°C.
- Determine E_a for the reaction.
- Given that the C—X bond energy is known to be about 325 kJ/mol, suggest a mechanism that explains the results in parts (a) and (c.)

Media Activities

- View the Reaction Rate and Concentration Visualization on the student CD. Is the order of HCL in the rate law a positive or a negative value (or equal to zero)? Explain how you know.
 - The rate law for a reaction must be determined from experiment (not from the coefficients in a balanced equation). One way to determine the rate law is by using the method of initial rates. Explain how this method works.
 - Consider the reaction between $NO(g)$ and $F_2(g)$. If doubling the concentration of NO (while keeping $[F_2]$ constant) causes the initial rate to increase by a factor of 2, then what is the order of NO in the rate law? From experiment, the order of F_2 in the rate law is 1. If the rate increases by a factor of 4, what happened to the concentration of F_2 if $[NO]$ was constant? If in a different reaction, tripling the concentration of some substance causes the rate to increase by a factor of nine, what would be the order of this substance? What is the relationship between concentration and the rate for a zero order reaction? For a reactant with -1 as the order?
- Most chemical reactions occur by a series of steps called a reaction mechanism. Open the Oscillating Reaction Visualization on the student CD to see an example of this. For simplicity, let's assume this is a two-step reaction. Step 1 is the formation of the blue solution and Step 2 is the formation of the clear solution. Which of these steps would be the rate-determining step in the mechanism? What is a rate-determining step?

- To review the various ideas associated with a mechanism, let's consider the following two-step mechanism for the depletion of ozone by NO :



What species is the intermediate? What species is the catalyst? What is a catalyst? What is the overall balanced equation? If Step 1 is the rate-determining step, what is the rate law derived from this mechanism? If you are having trouble answering these questions, review Sections 12.6 and 12.8 in the text. For some more problems with mechanisms, do Exercises 12.45, 12.47, and 12.48 in the text.

- For an introduction to the collision model, open the Gas Phase Reaction of NO and Cl_2 Visualization on the student CD. The product of the reaction is $ClNO$. What color sphere is N in the animation? O ? Cl ? The animation shows that only collisions of specific orientation result in product formation. Which collision orientation results in product formation? Give an example of a collision that would not result in product formation.
- For a more detailed review of the collision model, open the Transition States and Activation Energy Understanding Concepts activity on the student CD.
 - Review the general reaction coordinate diagram for an endothermic reaction in the activity. Sketch a general reaction coordinate diagram for an exothermic reaction indicating ΔH_{rxn} , $E_{a,f}$ and $E_{a,r}$. Is $E_{a,f}$ greater than or less than $E_{a,r}$ for an exothermic reaction? With all concentrations equal, which is slower, the forward or the reverse reaction for an exothermic reaction?
 - Click More Examples in the activity to see reaction coordinate diagrams for several reactions. For each example, determine ΔH_{rxn} from the activation energies given. For all these reactions, the rate of the forward reaction will increase as temperatures increases. Why?
 - Why does a catalyst speed up a reaction? Assuming the decomposition of C_2H_5Cl reaction can be catalyzed, sketch what the reaction coordinate diagram would look like for the catalyzed and uncatalyzed reaction. Show all the activation energies. Did ΔH_{rxn} change for the catalyzed reaction? For more practice with reaction coordinate diagrams, do Exercises 12.51 and 12.52 in the text.
- Test your understanding of Chapter 12 material by taking the ACE quizzes on the student web site.

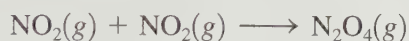


For additional web activities and other resources, visit the Zumdahl, *Chemistry*, Sixth Edition textbook site at <http://chemistry.college.hmco.com/students>.



Chemical Equilibrium

In doing stoichiometry calculations we assumed that reactions proceed to completion, that is, until one of the reactants runs out. Many reactions do proceed essentially to completion. For such reactions it can be assumed that the reactants are quantitatively converted to products and that the amount of limiting reactant that remains is negligible. On the other hand, there are many chemical reactions that stop far short of completion. An example is the dimerization of nitrogen dioxide:



The reactant, NO_2 , is a dark brown gas, and the product, N_2O_4 , is a colorless gas. When NO_2 is placed in an evacuated, sealed glass vessel at 25°C , the initial dark brown color decreases in intensity as it is converted to colorless N_2O_4 . However, even over a long period of time, the contents of the reaction vessel do not become colorless. Instead, the intensity of the brown color eventually becomes constant, which means that the concentration of NO_2 is no longer changing. This is illustrated on the molecular level in Fig. 13.1. This observation is a clear indication that the reaction has stopped short of completion. In fact, the system has reached **chemical equilibrium**, the state where the concentrations of all reactants and products remain constant with time.

Any chemical reactions carried out in a closed vessel will reach equilibrium. For some reactions the equilibrium position so favors the products

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13.1 The Equilibrium Condition

- The Characteristics of Chemical Equilibrium

13.2 The Equilibrium Constant

13.3 Equilibrium Expressions Involving Pressures

13.4 Heterogeneous Equilibria

13.5 Applications of the Equilibrium Constant

- The Extent of a Reaction
- Reaction Quotient
- Calculating Equilibrium Pressures and Concentrations

13.6 Solving Equilibrium Problems

- Treating Systems That Have Small Equilibrium Constants

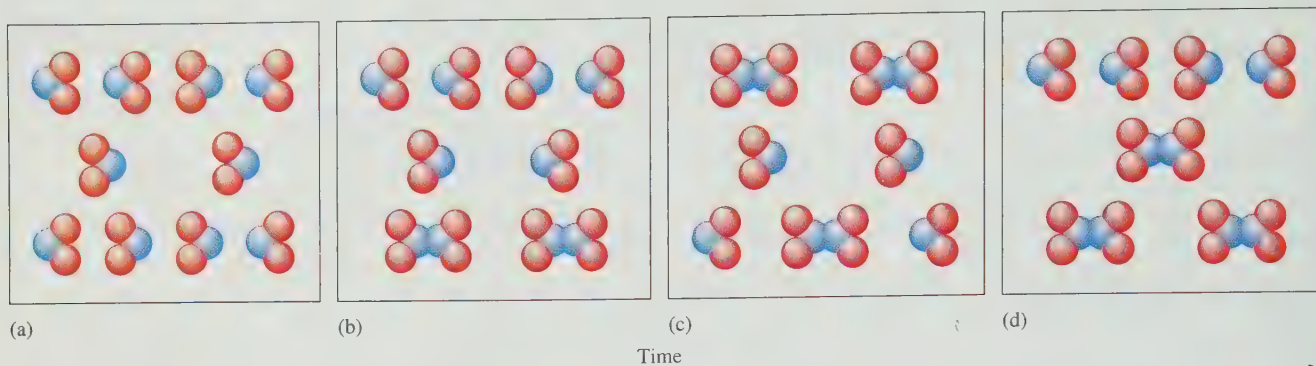
13.7 Le Châtelier's Principle

- The Effect of a Change in Concentration
- The Effect of a Change in Pressure
- The Effect of a Change in Temperature

The effect of temperature on the endothermic, aqueous equilibrium:



The violet solution in the center is at 25°C and contains significant quantities of both pink $\text{Co}(\text{H}_2\text{O})_6^{2+}$ and blue CoCl_4^{2-} . When the solution is cooled, it turns pink because the equilibrium is shifted to the left. Heating the solution favors the blue CoCl_4^{2-} ions.

**FIGURE 13.1**

A molecular representation of the reaction $2\text{NO}_2(g) \rightarrow \text{N}_2\text{O}_4(g)$ over time in a closed vessel. Note that the numbers of NO_2 and N_2O_4 in the container become constant (c and d) after sufficient time has passed.

that the reaction appears to have gone to completion. We say that the equilibrium position for such reactions lies *far to the right* (in the direction of the products). For example, when gaseous hydrogen and oxygen are mixed in stoichiometric quantities and react to form water vapor, the reaction proceeds essentially to completion. The amounts of the reactants that remain when the system reaches equilibrium are so tiny as to be negligible. By contrast, some reactions occur only to a slight extent. For example, when solid CaO is placed in a closed vessel at 25°C , the decomposition to solid Ca and gaseous O_2 is virtually undetectable. In cases like this, the equilibrium position is said to lie *far to the left* (in the direction of the reactants).

In this chapter we will discuss how and why a chemical system comes to equilibrium and the characteristics of equilibrium. In particular, we will discuss how to calculate the concentrations of the reactants and products present for a given system at equilibrium.

13.1 The Equilibrium Condition



Understanding Concepts: Equilibrium

Equilibrium is a dynamic situation.

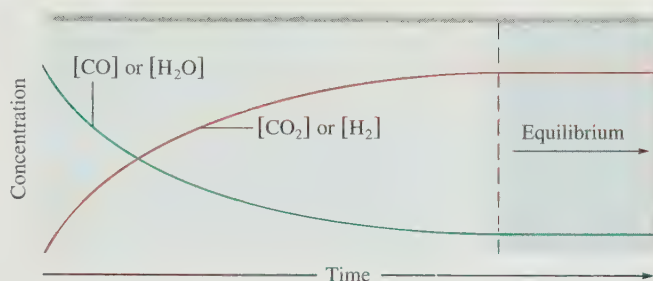
Since no changes occur in the concentrations of reactants or products in a reaction system at equilibrium, it may appear that everything has stopped. However, this is not the case. On the molecular level, there is frantic activity. Equilibrium is not static but is a highly *dynamic* situation. The concept of chemical equilibrium is analogous to the flow of cars across a bridge connecting two island cities. Suppose the traffic flow on the bridge is the same in both directions. It is obvious that there is motion, since one can see the cars traveling back and forth across the bridge, but the number of cars in each city is not changing because equal numbers of cars are entering and leaving. The result is no *net* change in the car population.

To see how this concept applies to chemical reactions, consider the reaction between steam and carbon monoxide in a closed vessel at a high temperature where the reaction takes place rapidly:



FIGURE 13.2

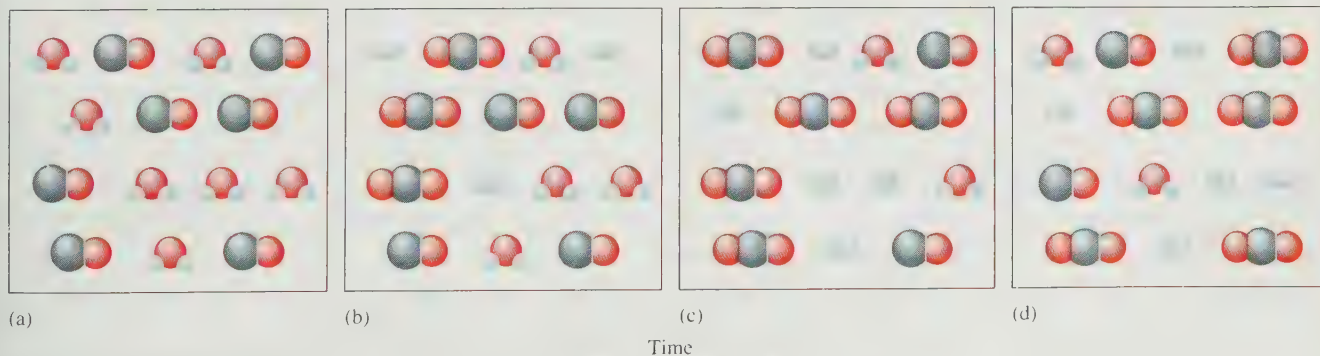
The changes in concentrations with time for the reaction $\text{H}_2\text{O}(g) + \text{CO}(g) \rightleftharpoons \text{H}_2(g) + \text{CO}_2(g)$ when equimolar quantities of $\text{H}_2\text{O}(g)$ and $\text{CO}(g)$ are mixed.



Assume that the same number of moles of gaseous CO and gaseous H_2O are placed in a closed vessel and allowed to react. The plots of the concentrations of reactants and products versus time are shown in Fig. 13.2. Note that since CO and H_2O were originally present in equal molar quantities, and since they react in a 1:1 ratio, the concentrations of the two gases are always equal. Also, since H_2 and CO_2 are formed in equal amounts, they are always present in the same concentrations.

Figure 13.2 is a profile of the progress of the reaction. When CO and H_2O are mixed, they immediately begin to react to form H_2 and CO_2 . This leads to a decrease in the concentrations of the reactants, but the concentrations of the products, which were initially at zero, are increasing. Beyond a certain time, indicated by the dashed line in Fig. 13.2, the concentrations of reactants and products no longer change—equilibrium has been reached. Unless the system is somehow disturbed, no further changes in concentrations will occur. Note that although the equilibrium position lies far to the right, the concentrations of reactants never go to zero; the reactants will always be present in small but constant concentrations. This is shown on the microscopic level in Fig. 13.3.

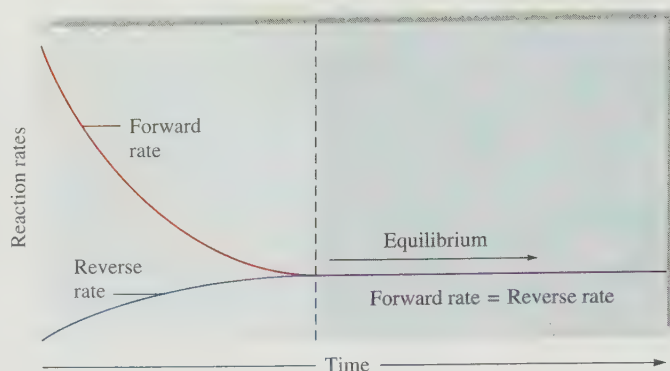
What would happen to the gaseous equilibrium mixture of reactants and products represented in Fig. 13.3, parts (c) and (d), if we injected some $\text{H}_2\text{O}(g)$ into the box? To answer this question, we need to be sure we understand the equilibrium condition: The concentrations of reactants and products remain constant at equilibrium because the forward and reverse reaction rates are equal. If we inject some H_2O molecules, what will happen to the forward reaction: $\text{H}_2\text{O} + \text{CO} \rightarrow \text{H}_2 + \text{CO}_2$? It will speed up because more H_2O molecules means more collisions between H_2O

**FIGURE 13.3**

(a) H_2O and CO are mixed in equal numbers and begin to react (b) to form CO_2 and H_2 . After time has passed, equilibrium is reached (c) and the numbers of reactant and product molecules then remain constant over time (d).

FIGURE 13.4

The changes with time in the rates of forward and reverse reactions for $\text{H}_2\text{O}(g) + \text{CO}(g) \rightleftharpoons \text{H}_2(g) + \text{CO}_2(g)$ when equimolar quantities of $\text{H}_2\text{O}(g)$ and $\text{CO}(g)$ are mixed. The rates do not change in the same way with time because the forward reaction has a much larger rate constant than the reverse reaction.

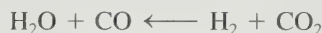


and CO molecules. This in turn will form more products and will cause the reverse reaction $\text{H}_2\text{O} + \text{CO} \leftarrow \text{H}_2 + \text{CO}_2$ to speed up. Thus the system will change until the forward and reverse reaction rates again become equal. Will this new equilibrium position contain more or fewer product molecules than are shown in Fig. 13.3(c) and (d)? Think about this carefully. If you are not sure of the answer now, keep reading. We will consider this type of situation in more detail later in this chapter.

Why does equilibrium occur? We saw in Chapter 12 that molecules react by colliding with one another, and the more collisions, the faster the reaction. This is why reaction rates depend on concentrations. In this case the concentrations of H_2O and CO are lowered by the forward reaction:



As the concentrations of the reactants decrease, the forward reaction slows down (Fig. 13.4). As in the bridge traffic analogy, there is also a reverse direction:

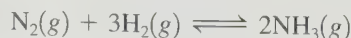


Initially in this experiment no H_2 and CO_2 were present, and this reverse reaction could not occur. However, as the forward reaction proceeds, the concentrations of H_2 and CO_2 build up, and the rate of the reverse reaction increases (Fig. 13.4) as the forward reaction slows down. Eventually, the concentrations reach levels where the rate of the forward reaction equals the rate of the reverse reaction. The system has reached equilibrium.

The equilibrium position of a reaction—left, right, or somewhere in between—is determined by many factors: the initial concentrations, the relative energies of the reactants and products, and the relative degree of “organization” of the reactants and products. Energy and organization come into play because nature tries to achieve minimum energy and maximum disorder, as we will show in detail in Chapter 16. For now, we will simply view the equilibrium phenomenon in terms of the rates of opposing reactions.

The Characteristics of Chemical Equilibrium

To explore the important characteristics of chemical equilibrium, we will consider the synthesis of ammonia from elemental nitrogen and hydrogen:



A double arrow ($\rightleftharpoons$) is used to show that a reaction can occur in either direction.

The relationship between equilibrium and thermodynamics is explored in Section 16.8.

The United States produces about 20 million tons of ammonia annually.

Molecules with strong bonds produce large activation energies and tend to react slowly at 25°C.

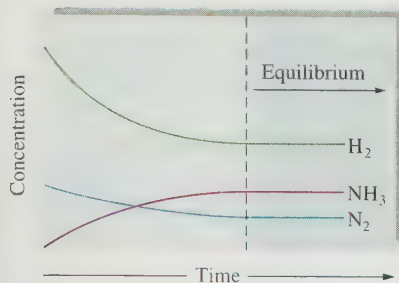


FIGURE 13.5

A concentration profile for the reaction $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ when only $\text{N}_2(\text{g})$ and $\text{H}_2(\text{g})$ are mixed initially.

This process is of great commercial value because ammonia is an important fertilizer for the growth of corn and other crops. Ironically, this beneficial process was discovered in Germany just before World War I in a search for ways to produce nitrogen-based explosives. In the course of this work, German chemist Fritz Haber (1868–1934) pioneered the large-scale production of ammonia.

When gaseous nitrogen, hydrogen, and ammonia are mixed in a closed vessel at 25°C, no apparent change in the concentrations occurs over time, regardless of the original amounts of the gases. Why? There are two possible reasons why the concentrations of the reactants and products of a given chemical reaction remain unchanged when mixed.

1. The system is at chemical equilibrium.
2. The forward and reverse reactions are so slow that the system moves toward equilibrium at a rate that cannot be detected.

The second reason applies to the nitrogen, hydrogen, and ammonia mixture at 25°C. As we saw in Chapters 8 and 9, the N_2 molecule has a very strong triple bond (941 kJ/mol) and thus is very unreactive. Also, the H_2 molecule has an unusually strong single bond (432 kJ/mol). Therefore, mixtures of N_2 , H_2 , and NH_3 at 25°C can exist with no apparent change over long periods of time, unless a catalyst is introduced to speed up the forward and reverse reactions. Under appropriate conditions, the system does reach equilibrium, as shown in Fig. 13.5. Note that because of the reaction stoichiometry, H_2 disappears three times as fast as N_2 does and NH_3 forms twice as fast as N_2 disappears.

13.2 The Equilibrium Constant

Science is fundamentally empirical—it is based on experiment. The development of the equilibrium concept is typical. From their observations of many chemical reactions, two Norwegian chemists, Cato Maximilian Guldberg (1836–1902) and Peter Waage (1833–1900), proposed in 1864 the **law of mass action** as a general description of the equilibrium condition. Guldberg and Waage postulated that for a reaction of the type



where A, B, C, and D represent chemical species and j , k , l , and m are their coefficients in the balanced equation, the law of mass action is represented by the following **equilibrium expression**:

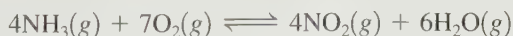
$$K = \frac{[\text{C}]^l[\text{D}]^m}{[\text{A}]^j[\text{B}]^k}$$

The square brackets indicate the concentrations of the chemical species *at equilibrium*, and K is a constant called the **equilibrium constant**.

SAMPLE EXERCISE 13.1

Writing Equilibrium Expressions

Write the equilibrium expression for the following reaction:



The law of mass action is based on experimental observation.

Applying the law of mass action gives

The square brackets indicate concentration in units of mol/L.

$$K = \frac{[\text{NO}_2]^4 [\text{H}_2\text{O}]^6}{[\text{NH}_3]^4 [\text{O}_2]^7}$$

Coefficient of NO₂ → 4
 Coefficient of H₂O → 6
 Coefficient of NH₃ → 4
 Coefficient of O₂ → 7

See Exercise 13.19.

The value of the equilibrium constant at a given temperature can be calculated if we know the equilibrium concentrations of the reaction components, as illustrated in Sample Exercise 13.2.

It is very important to note at this point that the equilibrium constants are customarily given without units. The reason for this is beyond the scope of this text, but it involves corrections for the nonideal behavior of the substances taking part in the reaction. When these corrections are made, the units cancel out and the corrected K has no units. Thus we will not use units for K in this text.

SAMPLE EXERCISE 13.2

Calculating the Values of K

The following equilibrium concentrations were observed for the Haber process at 127°C:

$$[\text{NH}_3] = 3.1 \times 10^{-2} \text{ mol/L}$$

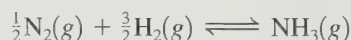
$$[\text{N}_2] = 8.5 \times 10^{-1} \text{ mol/L}$$

$$[\text{H}_2] = 3.1 \times 10^{-3} \text{ mol/L}$$

- Calculate the value of K at 127°C for this reaction.
- Calculate the value of the equilibrium constant at 127°C for the reaction

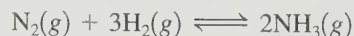


- Calculate the value of the equilibrium constant at 127°C for the reaction given by the equation



SOLUTION

- The balanced equation for the Haber process is



Thus

$$K = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(3.1 \times 10^{-2})^2}{(8.5 \times 10^{-1})(3.1 \times 10^{-3})^3} = 3.8 \times 10^4$$

Note that K is written without units.

- This reaction is written in the reverse order from the equation given in part a. This leads to the equilibrium expression

$$K' = \frac{[\text{N}_2][\text{H}_2]^3}{[\text{NH}_3]^2}$$

which is the reciprocal of the expression used in part a. Therefore,

$$K' = \frac{[\text{N}_2][\text{H}_2]^3}{[\text{NH}_3]^2} = \frac{1}{K} = \frac{1}{3.8 \times 10^4} = 2.6 \times 10^{-5}$$

c. We use the law of mass action:

$$K'' = \frac{[\text{NH}_3]}{[\text{N}_2]^{1/2}[\text{H}_2]^{3/2}}$$

If we compare this expression to that obtained in part a, we see that since

$$\frac{[\text{NH}_3]}{[\text{N}_2]^{1/2}[\text{H}_2]^{3/2}} = \left(\frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} \right)^{1/2}$$

$$K'' = K^{1/2}$$

Thus

$$K'' = K^{1/2} = (3.8 \times 10^4)^{1/2} = 1.9 \times 10^2$$

See Exercises 13.21 and 13.23 through 13.26.

We can draw some important conclusions from the results of Sample Exercise 13.2. For a reaction of the form



the equilibrium expression is

$$K = \frac{[\text{C}]^l[\text{D}]^m}{[\text{A}]^j[\text{B}]^k}$$

If this reaction is reversed, then the new equilibrium expression is

$$K' = \frac{[\text{A}]^j[\text{B}]^k}{[\text{C}]^l[\text{D}]^m} = \frac{1}{K}$$

If the original reaction is multiplied by some factor n to give



the equilibrium expression becomes

$$K'' = \frac{[\text{C}]^{nl}[\text{D}]^{nm}}{[\text{A}]^{nj}[\text{B}]^{nk}} = K^n$$

We Can Summarize These Conclusions About the Equilibrium Expression as Follows:

- The equilibrium expression for a reaction is the reciprocal of that for the reaction written in reverse.
- When the balanced equation for a reaction is multiplied by a factor n , the equilibrium expression for the new reaction is the original expression raised to the n th power. Thus $K_{\text{new}} = (K_{\text{original}})^n$.
- K values are customarily written without units.

The law of mass action applies to solution and gaseous equilibria.



A cross section showing how anhydrous ammonia is injected into the soil to act as a fertilizer.

For a reaction at a given temperature, there are many equilibrium positions but only one value for K .

The law of mass action is widely applicable. It correctly describes the equilibrium behavior of an amazing variety of chemical systems in solution and in the gas phase. Although, as we will see later, corrections must be applied in certain cases, such as for concentrated aqueous solutions and for gases at high pressures, the law of mass action provides a remarkably accurate description of all types of chemical equilibria.

Consider again the ammonia synthesis reaction. The equilibrium constant K always has the same value at a given temperature. At 500°C the value of K is 6.0×10^{-2} . Whenever N_2 , H_2 , and NH_3 are mixed together at this temperature, the system will always come to an equilibrium position such that

$$\frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = 6.0 \times 10^{-2}$$

This expression has the same value at 500°C , regardless of the amounts of the gases that are mixed together initially.

Although the special ratio of products to reactants defined by the equilibrium expression is constant for a given reaction system at a given temperature, the *equilibrium concentrations will not always be the same*. Table 13.1 gives three sets of data for the synthesis of ammonia, showing that even though the individual sets of equilibrium concentrations are quite different for the different situations, the *equilibrium constant, which depends on the ratio of the concentrations, remains the same* (within experimental error). Note that subscript zeros indicate initial concentrations.

Each set of *equilibrium concentrations* is called an **equilibrium position**. It is essential to distinguish between the equilibrium constant and the equilibrium positions for a given reaction system. There is only *one* equilibrium constant for a particular system at a particular temperature, but there are an *infinite* number of equilibrium positions. The specific equilibrium position adopted by a system depends on the initial concentrations, but the equilibrium constant does not.

TABLE 13.1 Results of Three Experiments for the Reaction $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$

Experiment	Initial Concentrations	Equilibrium Concentrations	$K = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$
I	$[\text{N}_2]_0 = 1.000\text{ M}$ $[\text{H}_2]_0 = 1.000\text{ M}$ $[\text{NH}_3]_0 = 0$	$[\text{N}_2] = 0.921\text{ M}$ $[\text{H}_2] = 0.763\text{ M}$ $[\text{NH}_3] = 0.157\text{ M}$	$K = 6.02 \times 10^{-2}$
II	$[\text{N}_2]_0 = 0$ $[\text{H}_2]_0 = 0$ $[\text{NH}_3]_0 = 1.000\text{ M}$	$[\text{N}_2] = 0.399\text{ M}$ $[\text{H}_2] = 1.197\text{ M}$ $[\text{NH}_3] = 0.203\text{ M}$	$K = 6.02 \times 10^{-2}$
III	$[\text{N}_2]_0 = 2.00\text{ M}$ $[\text{H}_2]_0 = 1.00\text{ M}$ $[\text{NH}_3]_0 = 3.00\text{ M}$	$[\text{N}_2] = 2.59\text{ M}$ $[\text{H}_2] = 2.77\text{ M}$ $[\text{NH}_3] = 1.82\text{ M}$	$K = 6.02 \times 10^{-2}$

SAMPLE EXERCISE 13.3

Equilibrium Positions

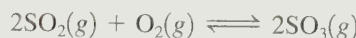
The following results were collected for two experiments involving the reaction at 600°C between gaseous sulfur dioxide and oxygen to form gaseous sulfur trioxide:

Experiment 1		Experiment 2	
Initial	Equilibrium	Initial	Equilibrium
$[\text{SO}_2]_0 = 2.00 \text{ M}$	$[\text{SO}_2] = 1.50 \text{ M}$	$[\text{SO}_2]_0 = 0.500 \text{ M}$	$[\text{SO}_2] = 0.590 \text{ M}$
$[\text{O}_2]_0 = 1.50 \text{ M}$	$[\text{O}_2] = 1.25 \text{ M}$	$[\text{O}_2]_0 = 0$	$[\text{O}_2] = 0.0450 \text{ M}$
$[\text{SO}_3]_0 = 3.00 \text{ M}$	$[\text{SO}_3] = 3.50 \text{ M}$	$[\text{SO}_3]_0 = 0.350 \text{ M}$	$[\text{SO}_3] = 0.260 \text{ M}$

Show that the equilibrium constant is the same in both cases.

SOLUTION

The balanced equation for the reaction is



From the law of mass action,

$$K = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]}$$

For Experiment 1,

$$K_1 = \frac{(3.50)^2}{(1.50)^2(1.25)} = 4.36$$

For Experiment 2,

$$K_2 = \frac{(0.260)^2}{(0.590)^2(0.0450)} = 4.32$$

The value of K is constant, within experimental error.

See Question 13.11.

13.3 Equilibrium Expressions Involving Pressures

So far we have been describing equilibria involving gases in terms of concentrations. Equilibria involving gases also can be described in terms of pressures. The relationship between the pressure and the concentration of a gas can be seen from the ideal gas equation:

$$PV = nRT \quad \text{or} \quad P = \left(\frac{n}{V}\right)RT = CRT$$

where C equals n/V , or the number of moles n of gas per unit volume V . Thus C represents the *molar concentration of the gas*.

For the ammonia synthesis reaction, the equilibrium expression can be written in terms of concentrations, that is,

$$K = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{C_{\text{NH}_3}^2}{(C_{\text{N}_2})(C_{\text{H}_2})^3} = K_c$$

The ideal gas equation was discussed in Section 5.3.

or in terms of the *equilibrium partial pressures of the gases*, that is,

$$K_p = \frac{P_{\text{NH}_3}^2}{(P_{\text{N}_2})(P_{\text{H}_2}^3)}$$

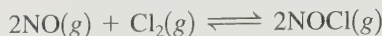
K involves concentrations; K_p involves pressures. In some books, the symbol K_c is used instead of K .

Both the symbols K and K_c are used commonly for an equilibrium constant in terms of concentrations. We will always use K in this book. The symbol K_p represents an equilibrium constant in terms of partial pressures.

SAMPLE EXERCISE 13.4

Calculating Values of K_p

The reaction for the formation of nitrosyl chloride



was studied at 25°C. The pressures at equilibrium were found to be

$$P_{\text{NOCl}} = 1.2 \text{ atm}$$

$$P_{\text{NO}} = 5.0 \times 10^{-2} \text{ atm}$$

$$P_{\text{Cl}_2} = 3.0 \times 10^{-1} \text{ atm}$$

Calculate the value of K_p for this reaction at 25°C.

SOLUTION

For this reaction,

$$\begin{aligned} K_p &= \frac{P_{\text{NOCl}}^2}{(P_{\text{NO}})^2(P_{\text{Cl}_2})} = \frac{(1.2)^2}{(5.0 \times 10^{-2})^2(3.0 \times 10^{-1})} \\ &= 1.9 \times 10^3 \end{aligned}$$

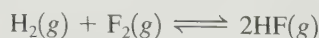
See Exercises 13.27 and 13.28.

The relationship between K and K_p for a particular reaction follows from the fact that for an ideal gas, $C = P/RT$. For example, for the ammonia synthesis reaction,

$$P = CRT \quad \text{or} \quad C = \frac{P}{RT}$$

$$\begin{aligned} K &= \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{C_{\text{NH}_3}^2}{(C_{\text{N}_2})(C_{\text{H}_2}^3)} \\ &= \frac{\left(\frac{P_{\text{NH}_3}}{RT}\right)^2}{\left(\frac{P_{\text{N}_2}}{RT}\right)\left(\frac{P_{\text{H}_2}}{RT}\right)^3} = \frac{P_{\text{NH}_3}^2}{(P_{\text{N}_2})(P_{\text{H}_2}^3)} \times \frac{\left(\frac{1}{RT}\right)^2}{\left(\frac{1}{RT}\right)^4} \\ &= \frac{P_{\text{NH}_3}^2}{(P_{\text{N}_2})(P_{\text{H}_2}^3)} (RT)^2 \\ &= K_p(RT)^2 \end{aligned}$$

However, for the synthesis of hydrogen fluoride from its elements,



the relationship between K and K_p is given by

$$K = \frac{[\text{HF}]^2}{[\text{H}_2][\text{F}_2]} = \frac{C_{\text{HF}}^2}{(C_{\text{H}_2})(C_{\text{F}_2})}$$

$$\begin{aligned}
 &= \frac{\left(\frac{P_{\text{HF}}}{RT}\right)^2}{\left(\frac{P_{\text{H}_2}}{RT}\right)\left(\frac{P_{\text{F}_2}}{RT}\right)} = \frac{P_{\text{HF}}^2}{(P_{\text{H}_2})(P_{\text{F}_2})} \\
 &= K_p
 \end{aligned}$$

Thus, for this reaction, K is equal to K_p . This equality occurs because the sum of the coefficients on either side of the balanced equation is identical, so the terms in RT cancel out. In the equilibrium expression for the ammonia synthesis reaction, the sum of the powers in the numerator is different from that in the denominator, and K does not equal K_p .

For the general reaction



the relationship between K and K_p is

$$K_p = K(RT)^{\Delta n}$$

where Δn is the sum of the coefficients of the *gaseous* products minus the sum of the coefficients of the *gaseous* reactants. This equation is quite easy to derive from the definitions of K and K_p and the relationship between pressure and concentration. For the preceding general reaction,

$$\begin{aligned}
 K_p &= \frac{(P_{\text{C}})^l(P_{\text{D}})^m}{(P_{\text{A}})^j(P_{\text{B}})^k} = \frac{(C_{\text{C}} \times RT)^l(C_{\text{D}} \times RT)^m}{(C_{\text{A}} \times RT)^j(C_{\text{B}} \times RT)^k} \\
 &= \frac{(C_{\text{C}})^l(C_{\text{D}})^m}{(C_{\text{A}})^j(C_{\text{B}})^k} \times \frac{(RT)^{l+m}}{(RT)^{j+k}} = K(RT)^{(l+m)-(j+k)} \\
 &= K(RT)^{\Delta n}
 \end{aligned}$$

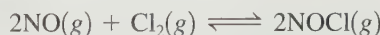
Δn always involves products minus reactants.

where $\Delta n = (l + m) - (j + k)$, the difference in the sums of the coefficients for the gaseous products and reactants.

SAMPLE EXERCISE 13.5

Calculating K from K_p

Using the value of K_p obtained in Sample Exercise 13.4, calculate the value of K at 25°C for the reaction



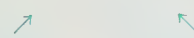
SOLUTION

From the value of K_p , we can calculate K using

$$K_p = K(RT)^{\Delta n}$$

where $T = 25 + 273 = 298 \text{ K}$ and

$$\Delta n = 2 - (2 + 1) = -1$$



Sum of
product
coefficients

Sum of
reactant
coefficients

Thus

$$K_p = K(RT)^{\Delta n} = \frac{K}{RT}$$

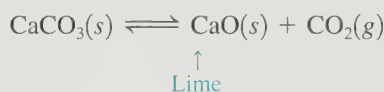
and

$$\begin{aligned} K &= K_p(RT) \\ &= (1.9 \times 10^3)(0.08206)(298) \\ &= 4.6 \times 10^4 \end{aligned}$$

See Exercises 13.29 and 13.30.

13.4 Heterogeneous Equilibria

So far we have discussed equilibria only for systems in the gas phase, where all reactants and products are gases. These are **homogeneous equilibria**. However, many equilibria involve more than one phase and are called **heterogeneous equilibria**. For example, the thermal decomposition of calcium carbonate in the commercial preparation of lime occurs by a reaction involving both solid and gas phases:



Straightforward application of the law of mass action leads to the equilibrium expression

$$K' = \frac{[\text{CO}_2][\text{CaO}]}{[\text{CaCO}_3]}$$

However, experimental results show that the *position of a heterogeneous equilibrium does not depend on the amounts of pure solids or liquids present* (see Fig. 13.6). The fundamental reason for this behavior is that the concentrations of pure solids and liquids cannot change. Thus the equilibrium expression for the decomposition of solid calcium carbonate might be represented as

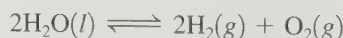
$$K' = \frac{[\text{CO}_2]C_1}{C_2}$$

where C_1 and C_2 are constants representing the concentrations of the solids CaO and CaCO_3 , respectively. This expression can be rearranged to give

$$\frac{C_2 K'}{C_1} = K = [\text{CO}_2]$$

We can generalize from this result as follows: If pure solids or pure liquids are involved in a chemical reaction, their concentrations *are not included in the equilibrium expression* for the reaction. This simplification occurs *only* with pure solids or liquids, not with solutions or gases, since in these last two cases the concentrations can vary.

For example, in the decomposition of liquid water to gaseous hydrogen and oxygen,

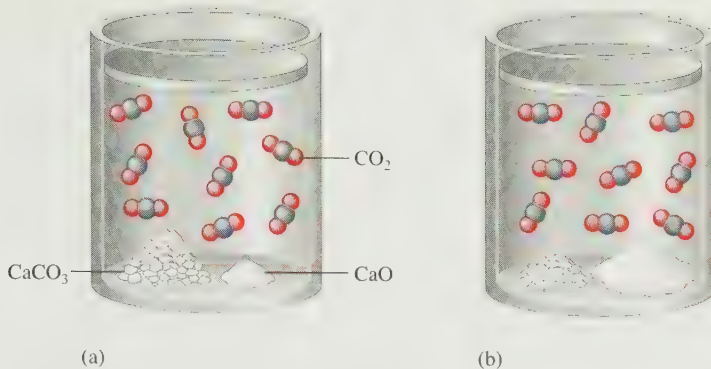


Lime is among the top five chemicals manufactured in the United States in terms of the amount produced.

The concentrations of pure liquids and solids are constant.



The Seven Sisters chalk cliffs in East Sussex, England. The chalk is made up of compressed calcium carbonate skeletons of microscopic algae from the late Cretaceous Period.

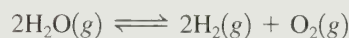
**FIGURE 13.6**

The position of the equilibrium $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ does not depend on the amounts of $\text{CaCO}_3(\text{s})$ and $\text{CaO}(\text{s})$ present.

where

$$K = [\text{H}_2]^2[\text{O}_2] \quad \text{and} \quad K_p = (P_{\text{H}_2})^2(P_{\text{O}_2})$$

water is not included in either equilibrium expression because it is a pure liquid. However, if the reaction were carried out under conditions where the water is a gas rather than a liquid, that is,



then

$$K = \frac{[\text{H}_2]^2[\text{O}_2]}{[\text{H}_2\text{O}]^2} \quad \text{and} \quad K_p = \frac{(P_{\text{H}_2})^2(P_{\text{O}_2})}{P_{\text{H}_2\text{O}}^2}$$

because the concentration or pressure of water vapor can change.

SAMPLE EXERCISE 13.6

Equilibrium Expressions for Heterogeneous Equilibria

Write the expressions for K and K_p for the following processes:

- The decomposition of solid phosphorus pentachloride to liquid phosphorus trichloride and chlorine gas.
- Deep blue solid copper(II) sulfate pentahydrate is heated to drive off water vapor to form white solid copper(II) sulfate.



Hydrated copper(II) sulfate on the left. Water applied to anhydrous copper(II) sulfate, on the right, forms the hydrated compound.

SOLUTION

a. The reaction is



The equilibrium expressions are

$$K = [\text{Cl}_2] \quad \text{and} \quad K_p = P_{\text{Cl}_2}$$

In this case neither the pure solid PCl_5 nor the pure liquid PCl_3 is included in the equilibrium expressions.

b. The reaction is



The equilibrium expressions are

$$K = [\text{H}_2\text{O}]^5 \quad \text{and} \quad K_p = (P_{\text{H}_2\text{O}})^5$$

The solids are not included.

See Exercise 13.31.

13.5 Applications of the Equilibrium Constant

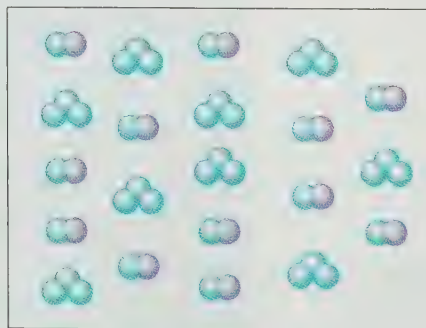
Knowing the equilibrium constant for a reaction allows us to predict several important features of the reaction: the tendency of the reaction to occur (but not the speed of the reaction), whether a given set of concentrations represents an equilibrium condition, and the equilibrium position that will be achieved from a given set of initial concentrations.

To introduce some of these ideas, we will first consider the reaction



where and represent two different types of atoms. Assume that this reaction has an equilibrium constant equal to 16.

In a given experiment, the two types of molecules are mixed together in the following amounts:



After the system reacts and comes to equilibrium, what will the system look like? We know that at equilibrium the ratio

$$\frac{(N_{\text{H}_2})(N_{\text{O}_2})}{(N_{\text{H}_2\text{O}})(N_{\text{H}_2\text{O}})} = 16$$

must be satisfied, where each N represents the number of molecules of each type. We originally have 9  molecules and 12  molecules. As a place to start, let's just assume that 5  molecules disappear for the system to reach equilibrium. Since equal numbers of the  and  molecules react, this means that 5  molecules also will disappear. This also means that 5  molecules and 5  molecules will be formed. We can summarize as follows:

<i>Initial Conditions</i>	<i>New Conditions</i>
9  molecules	$9 - 5 = 4$  molecules
12  molecules	$12 - 5 = 7$  molecules
0  molecules	$0 + 5 = 5$  molecules
0  molecules	$0 + 5 = 5$  molecules

Do the new conditions represent equilibrium for this reaction system? We can find out by taking the ratio of the numbers of molecules:

$$\frac{(N_{\text{H}_2})(N_{\text{O}_2})}{(N_{\text{H}_2\text{O}})(N_{\text{H}_2\text{O}})} = \frac{(5)(5)}{(4)(7)} = 0.9$$

Thus this is not an equilibrium position because the ratio is not 16, as required for equilibrium. In which direction must the system move to achieve equilibrium? Since the observed ratio is smaller than 16, we must increase the numerator and decrease the denominator: The system needs to move to the right (toward more products) to achieve equilibrium. That is, more than 5 of the original reactant molecules must disappear to reach equilibrium for this system. How can we find the correct number? Since we do not know the number of molecules that need to disappear to reach equilibrium, let's call this number x . Now we can set up a table similar to the one we used earlier:

<i>Initial Conditions</i>		<i>Equilibrium Conditions</i>
9  molecules	x  disappear	$9 - x$  molecules
12  molecules	x  disappear	$12 - x$  molecules
0  molecules	x  form	x  molecules
0  molecules	x  form	x  molecules

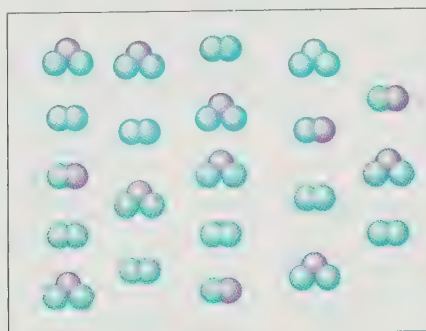
For the system to be at equilibrium, we know that the following ratio must be satisfied:

$$\frac{(N_{\text{H}_2})(N_{\text{O}_2})}{(N_{\text{H}_2\text{O}})(N_{\text{H}_2\text{O}})} = 16 = \frac{(x)(x)}{(9-x)(12-x)}$$

The easiest way to solve for x here is by trial and error. From our previous discussion we know that x is greater than 5. Also, we know that it must be less than 9 because we have only 9  molecules to start. We can't use all of them or we will have a zero in the denominator, which causes the ratio to be infinitely large. By trial and error, we find that $x = 8$ because

$$\frac{(x)(x)}{(9-x)(12-x)} = \frac{(8)(8)}{(9-8)(12-8)} = \frac{64}{4} = 16$$

The equilibrium mixture can be pictured as follows:



Note that it contains 8  molecules, 8  molecules, 1  molecule, and 4  molecules as required.

This pictorial example should help you understand the fundamental ideas of equilibrium. Now we will proceed to a more systematic quantitative treatment of chemical equilibrium.

The Extent of a Reaction

The inherent tendency for a reaction to occur is indicated by the magnitude of the equilibrium constant. A value of K much larger than 1 means that at equilibrium the reaction system will consist of mostly products—the equilibrium lies to the right. Another way of saying this is that reactions with very large equilibrium constants go essentially to completion. On the other hand, a very small value of K means that the system at equilibrium will consist of mostly reactants—the equilibrium position is far to the left. The given reaction does not occur to any significant extent.

It is important to understand that *the size of K and the time required to reach equilibrium are not directly related*. The time required to achieve equilibrium depends on the reaction rate, which is determined by the size of the activation energy. The size of K is determined by thermodynamic factors such as the difference in energy between products and reactants. This difference is represented in Fig. 13.7 and will be discussed in detail in Chapter 16.

Reaction Quotient

When the reactants and products of a given chemical reaction are mixed, it is useful to know whether the mixture is at equilibrium or, if not, the direction in which the system must shift to reach equilibrium. If the concentration of one of the reactants or products is zero, the system will shift in the direction that produces the missing component. However, if all the initial concentrations are nonzero, it is more difficult to determine the direction of the move toward equilibrium. To determine

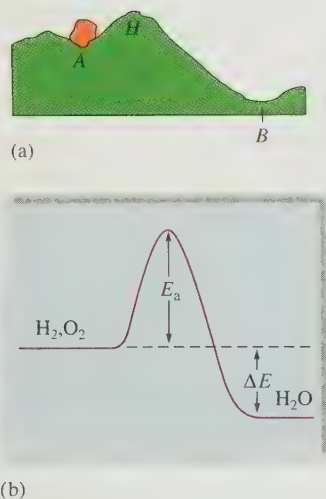
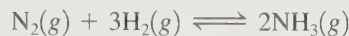


FIGURE 13.7

(a) A physical analogy illustrating the difference between thermodynamic and kinetic stabilities. The boulder is thermodynamically more stable (lower potential energy) in position B than in position A but cannot get over the hump H . (b) The reactants H_2 and O_2 have a strong tendency to form H_2O . That is, H_2O has lower energy than H_2 and O_2 . However, the large activation energy E_a prevents the reaction at 25°C . In other words, the magnitude of K for the reaction depends on ΔE , but the reaction rate depends on E_a .

the shift in such cases, we use the **reaction quotient** Q . The reaction quotient is obtained by applying the law of mass action using *initial concentrations* instead of equilibrium concentrations. For example, for the synthesis of ammonia



the expression for the reaction quotient is

$$Q = \frac{[\text{NH}_3]_0^2}{[\text{N}_2]_0[\text{H}_2]_0^3}$$

where the subscript zeros indicate initial concentrations.

To determine in which direction a system will shift to reach equilibrium, we compare the values of Q and K . There are three possible cases:

1. Q is equal to K . The system is at equilibrium; no shift will occur.
2. Q is greater than K . In this case, the ratio of initial concentrations of products to initial concentrations of reactants is too large. To reach equilibrium, a net change of products to reactants must occur. The system *shifts to the left*, consuming products and forming reactants, until equilibrium is achieved.
3. Q is less than K . In this case, the ratio of initial concentrations of products to initial concentrations of reactants is too small. The system *must shift to the right*, consuming reactants and forming products, to attain equilibrium.

SAMPLE EXERCISE 13.7

Using the Reaction Quotient

For the synthesis of ammonia at 500°C, the equilibrium constant is 6.0×10^{-2} . Predict the direction in which the system will shift to reach equilibrium in each of the following cases:

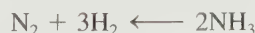
- a. $[\text{NH}_3]_0 = 1.0 \times 10^{-3} M$; $[\text{N}_2]_0 = 1.0 \times 10^{-5} M$; $[\text{H}_2]_0 = 2.0 \times 10^{-3} M$
- b. $[\text{NH}_3]_0 = 2.00 \times 10^{-4} M$; $[\text{N}_2]_0 = 1.50 \times 10^{-5} M$; $[\text{H}_2]_0 = 3.54 \times 10^{-1} M$
- c. $[\text{NH}_3]_0 = 1.0 \times 10^{-4} M$; $[\text{N}_2]_0 = 5.0 M$; $[\text{H}_2]_0 = 1.0 \times 10^{-2} M$

SOLUTION

- a. First we calculate the value of Q :

$$\begin{aligned} Q &= \frac{[\text{NH}_3]_0^2}{[\text{N}_2]_0[\text{H}_2]_0^3} = \frac{(1.0 \times 10^{-3})^2}{(1.0 \times 10^{-5})(2.0 \times 10^{-3})^3} \\ &= 1.3 \times 10^7 \end{aligned}$$

Since $K = 6.0 \times 10^{-2}$, Q is much greater than K . To attain equilibrium, the concentrations of the products must be decreased and the concentrations of the reactants increased. The system will shift to the left:



- b. We calculate the value of Q :

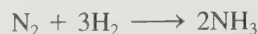
$$\begin{aligned} Q &= \frac{[\text{NH}_3]_0^2}{[\text{N}_2]_0[\text{H}_2]_0^3} = \frac{(2.00 \times 10^{-4})^2}{(1.50 \times 10^{-5})(3.54 \times 10^{-1})^3} \\ &= 6.01 \times 10^{-2} \end{aligned}$$

In this case $Q = K$, so the system is at equilibrium. No shift will occur.

c. The value of Q is

$$Q = \frac{[\text{NH}_3]_0^2}{[\text{N}_2]_0[\text{H}_2]_0^3} = \frac{(1.0 \times 10^{-4})^2}{(5.0)(1.0 \times 10^{-2})^3} = 2.0 \times 10^{-3}$$

Here Q is less than K , so the system will shift to the right to attain equilibrium by increasing the concentration of the product and decreasing the reactant concentrations:

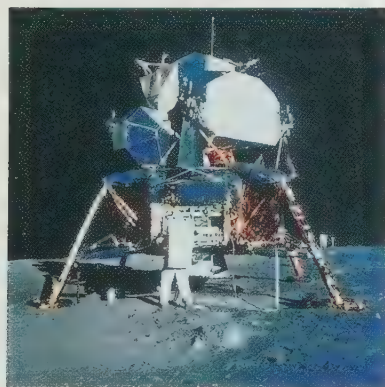


See Exercises 13.35 through 13.38.

Calculating Equilibrium Pressures and Concentrations

A typical equilibrium problem involves finding the equilibrium concentrations (or pressures) of reactants and products, given the value of the equilibrium constant and the initial concentrations (or pressures). However, since such problems sometimes become complicated mathematically, we will develop useful strategies for solving them by considering cases for which we know one or more of the equilibrium concentrations (or pressures).

SAMPLE EXERCISE 13.8



Apollo II lunar landing module at Tranquility Base, 1969.

Calculating Equilibrium Pressures I

Dinitrogen tetroxide in its liquid state was used as one of the fuels on the lunar lander for the NASA Apollo missions. In the gas phase it decomposes to gaseous nitrogen dioxide:



Consider an experiment in which gaseous N_2O_4 was placed in a flask and allowed to reach equilibrium at a temperature where $K_p = 0.133$. At equilibrium, the pressure of N_2O_4 was found to be 2.71 atm. Calculate the equilibrium pressure of $\text{NO}_2(g)$.

SOLUTION

We know that the equilibrium pressures of the gases NO_2 and N_2O_4 must satisfy the relationship

$$K_p = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}} = 0.133$$

Since we know $P_{\text{N}_2\text{O}_4}$, we can simply solve for P_{NO_2} :

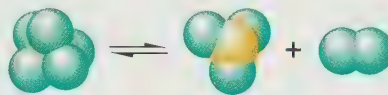
$$P_{\text{NO}_2}^2 = K_p(P_{\text{N}_2\text{O}_4}) = (0.133)(2.71) = 0.360$$

Therefore,

$$P_{\text{NO}_2} = \sqrt{0.360} = 0.600$$

See Exercises 13.39 and 13.40.

At a certain temperature a 1.00-L flask initially contained 0.298 mol $\text{PCl}_3(\text{g})$ and 8.70×10^{-3} mol $\text{PCl}_5(\text{g})$. After the system had reached equilibrium, 2.00×10^{-3} mol $\text{Cl}_2(\text{g})$ was found in the flask. Gaseous PCl_5 decomposes according to the reaction



Calculate the equilibrium concentrations of all species and the value of K .

SOLUTION

The equilibrium expression for this reaction is

$$K = \frac{[\text{Cl}_2][\text{PCl}_3]}{[\text{PCl}_5]}$$

To find the value of K , we must calculate the equilibrium concentrations of all species and then substitute these quantities into the equilibrium expression. The best method for finding the equilibrium concentrations is to begin with the initial concentrations, which we will define as the concentrations before any shift toward equilibrium has occurred. We will then modify these initial concentrations appropriately to find the equilibrium concentrations.

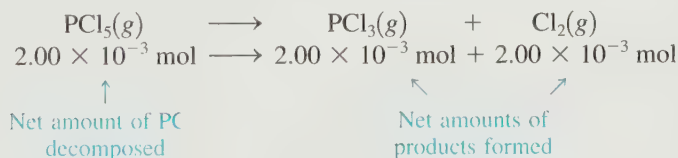
The initial concentrations are

$$[\text{Cl}_2]_0 = 0$$

$$[\text{PCl}_3]_0 = \frac{0.298 \text{ mol}}{1.00 \text{ L}} = 0.298 \text{ M}$$

$$[\text{PCl}_5]_0 = \frac{8.70 \times 10^{-3} \text{ mol}}{1.00 \text{ L}} = 8.70 \times 10^{-3} \text{ M}$$

Next we find the change required to reach equilibrium. Since no Cl_2 was initially present but $2.00 \times 10^{-3} \text{ M}$ Cl_2 is present at equilibrium, 2.00×10^{-3} mol PCl_5 must have decomposed to form 2.00×10^{-3} mol Cl_2 and 2.00×10^{-3} mol PCl_3 . In other words, to reach equilibrium, the reaction shifted to the right:



Now we apply this change to the initial concentrations to obtain the equilibrium concentrations:

$$[\text{Cl}_2] = \underbrace{0}_{[\text{Cl}_2]_0} + \frac{2.00 \times 10^{-3} \text{ mol}}{1.00 \text{ L}} = 2.00 \times 10^{-3} \text{ M}$$

$$[\text{PCl}_3] = \underbrace{0.298 \text{ M}}_{[\text{PCl}_3]_0} + \frac{2.00 \times 10^{-3} \text{ mol}}{1.00 \text{ L}} = 0.300 \text{ M}$$

$$[\text{PCl}_5] = \underbrace{8.70 \times 10^{-3} \text{ M}}_{[\text{PCl}_5]_0} - \frac{2.00 \times 10^{-3} \text{ mol}}{1.00 \text{ L}} = 6.70 \times 10^{-3} \text{ M}$$

These equilibrium concentrations can now be used to find K :

$$K = \frac{[\text{Cl}_2][\text{PCl}_3]}{[\text{PCl}_5]} = \frac{(2.00 \times 10^{-3})(0.300)}{6.70 \times 10^{-3}} = 8.96 \times 10^{-2}$$

See Exercises 13.41 through 13.44.

Sometimes we are not given any of the equilibrium concentrations (or pressures), only the initial values. Then we must use the stoichiometry of the reaction to express concentrations (or pressures) at equilibrium in terms of the initial values. This is illustrated in Sample Exercise 13.10.

SAMPLE EXERCISE 13.10

Calculating Equilibrium Concentrations I

Carbon monoxide reacts with steam to produce carbon dioxide and hydrogen. At 700 K the equilibrium constant is 5.10. Calculate the equilibrium concentrations of all species if 1.000 mol of each component is mixed in a 1.000-L flask.

SOLUTION

The balanced equation for the reaction is



and

$$K = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]} = 5.10$$

Next we calculate the initial concentrations:

$$[\text{CO}]_0 = [\text{H}_2\text{O}]_0 = [\text{CO}_2]_0 = [\text{H}_2]_0 = \frac{1.000 \text{ mol}}{1.000 \text{ L}} = 1.000 \text{ M}$$

Is the system at equilibrium, and if not, which way will it shift to reach the equilibrium position? These questions can be answered by calculating Q :

$$Q = \frac{[\text{CO}_2]_0[\text{H}_2]_0}{[\text{CO}]_0[\text{H}_2\text{O}]_0} = \frac{(1.000 \text{ mol/L})(1.000 \text{ mol/L})}{(1.000 \text{ mol/L})(1.000 \text{ mol/L})} = 1.000$$

Since Q is less than K , the system is not at equilibrium initially but must shift to the right.

What are the equilibrium concentrations? As before, we start with the initial concentrations and modify them to obtain the equilibrium concentrations. We must ask this question: How much will the system shift to the right to attain the equilibrium condition? In Sample Exercise 13.9 the change needed for the system to reach equilibrium was given. However, in this case we do not have this information.

Since the required change in concentrations is unknown at this point, we will define it in terms of x . Let's assume that x mol/L CO must react for the system to reach equilibrium. This means that the initial concentration of CO will decrease by x mol/L:

$$[\text{CO}] = [\text{CO}]_0 - x$$

$\uparrow \qquad \qquad \uparrow \qquad \qquad \uparrow$
 Equilibrium Initial Change

Since each CO molecule reacts with one H₂O molecule, the concentration of water vapor also must decrease by x mol/L:

$$[\text{H}_2\text{O}] = [\text{H}_2\text{O}]_0 - x$$

As the reactant concentrations decrease, the product concentrations increase. Since all the coefficients are 1 in the balanced reaction, 1 mol CO reacting with 1 mol H₂O will produce 1 mol CO₂ and 1 mol H₂. Or in the present case, to reach equilibrium, x mol/L CO will react with x mol/L H₂O to give an additional x mol/L CO₂ and x mol/L H₂:



Thus the initial concentrations of CO₂ and H₂ will increase by x mol/L:

$$\begin{aligned} [\text{CO}_2] &= [\text{CO}_2]_0 + x \\ [\text{H}_2] &= [\text{H}_2]_0 + x \end{aligned}$$

Now we have all the equilibrium concentrations defined in terms of the initial concentrations and the change x :

Initial Concentration (mol/L)	Change (mol/L)	Equilibrium Concentration (mol/L)
$[\text{CO}]_0 = 1.000$	$-x$	$1.000 - x$
$[\text{H}_2\text{O}]_0 = 1.000$	$-x$	$1.000 - x$
$[\text{CO}_2]_0 = 1.000$	$+x$	$1.000 + x$
$[\text{H}_2]_0 = 1.000$	$+x$	$1.000 + x$

Note that the sign of x is determined by the direction of the shift. In this example, the system shifts to the right, so the product concentrations increase and the reactant concentrations decrease. Also note that because the coefficients in the balanced equation are all 1, the magnitude of the change is the same for all species.

Now since we know that the equilibrium concentrations must satisfy the equilibrium expression, we can find the value of x by substituting these concentrations into the expression

$$K = 5.10 = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]} = \frac{(1.000 + x)(1.000 + x)}{(1.000 - x)(1.000 - x)} = \frac{(1.000 + x)^2}{(1.000 - x)^2}$$

Since the right side of the equation is a perfect square, the solution of the problem can be simplified by taking the square root of both sides:

$$\sqrt{5.10} = 2.26 = \frac{1.000 + x}{1.000 - x}$$

Multiplying and collecting terms gives

$$x = 0.387 \text{ mol/L}$$

Thus the system shifts to the right, consuming 0.387 mol/L CO and 0.387 mol/L H₂O and forming 0.387 mol/L CO₂ and 0.387 mol/L H₂.

Now the equilibrium concentrations can be calculated:

$$\begin{aligned} [\text{CO}] &= [\text{H}_2\text{O}] = 1.000 - x = 1.000 - 0.387 = 0.613 \text{ M} \\ [\text{CO}_2] &= [\text{H}_2] = 1.000 + x = 1.000 + 0.387 = 1.387 \text{ M} \end{aligned}$$

CHECK:

These values can be checked by substituting them back into the equilibrium expression to make sure they give the correct value for K :

$$K = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]} = \frac{(1.387)^2}{(0.613)^2} = 5.12$$

This result is the same as the given value of K (5.10) within round-off error, so the answer must be correct.

See Exercise 13.45.

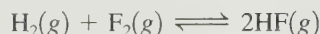
SAMPLE EXERCISE 13.11

Calculating Equilibrium Concentrations II

Assume that the reaction for the formation of gaseous hydrogen fluoride from hydrogen and fluorine has an equilibrium constant of 1.15×10^2 at a certain temperature. In a particular experiment, 3.000 mol of each component was added to a 1.500-L flask. Calculate the equilibrium concentrations of all species.

SOLUTION

The balanced equation for the reaction is



The equilibrium expression is

$$K = 1.15 \times 10^2 = \frac{[\text{HF}]^2}{[\text{H}_2][\text{F}_2]}$$

We first calculate the initial concentrations:

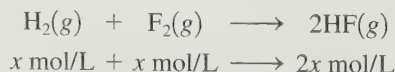
$$[\text{HF}]_0 = [\text{H}_2]_0 = [\text{F}_2]_0 = \frac{3.000 \text{ mol}}{1.500 \text{ L}} = 2.000 \text{ M}$$

Then we find the value of Q :

$$Q = \frac{[\text{HF}]_0^2}{[\text{H}_2]_0[\text{F}_2]_0} = \frac{(2.000)^2}{(2.000)(2.000)} = 1.000$$

Since Q is much less than K , the system must shift to the right to reach equilibrium.

What change in the concentrations is necessary? Since this is presently unknown, we will define the change needed in terms of x . Let x equal the number of moles per liter of H_2 consumed to reach equilibrium. The stoichiometry of the reaction shows that x mol/L F_2 also will be consumed and $2x$ mol/L HF will be formed:



Now the equilibrium concentrations can be expressed in terms of x :

Initial Concentration (mol/L)	Change (mol/L)	Equilibrium Concentration (mol/L)
$[\text{H}_2]_0 = 2.000$	$-x$	$[\text{H}_2] = 2.000 - x$
$[\text{F}_2]_0 = 2.000$	$-x$	$[\text{F}_2] = 2.000 - x$
$[\text{HF}]_0 = 2.000$	$+2x$	$[\text{HF}] = 2.000 + 2x$

We often refer to this form as an **ICE** table (indicated by the first letters of Initial, Change, and Equilibrium).

These concentrations can be represented in a shorthand table as follows:

	$\text{H}_2(\text{g})$	+	$\text{F}_2(\text{g})$	$\rightleftharpoons$	$2\text{HF}(\text{g})$
Initial:	2.000		2.000		2.000
Change:	$-x$		$-x$		$+2x$
Equilibrium:	$2.000 - x$		$2.000 - x$		$2.000 + 2x$

To solve for x , we substitute the equilibrium concentrations into the equilibrium expression:

$$K = 1.15 \times 10^2 = \frac{[\text{HF}]^2}{[\text{H}_2][\text{F}_2]} = \frac{(2.000 + 2x)^2}{(2.000 - x)^2}$$

The right side of this equation is a perfect square, so taking the square root of both sides gives

$$\sqrt{1.15 \times 10^2} = \frac{2.000 + 2x}{2.000 - x}$$

which yields $x = 1.528$. The equilibrium concentrations can now be calculated:

$$[\text{H}_2] = [\text{F}_2] = 2.000 \text{ M} - x = 0.472 \text{ M}$$

$$[\text{HF}] = 2.000 \text{ M} + 2x = 5.056 \text{ M}$$

CHECK:

Checking these values by substituting them into the equilibrium expression gives

$$\frac{[\text{HF}]^2}{[\text{H}_2][\text{F}_2]} = \frac{(5.056)^2}{(0.472)^2} = 1.15 \times 10^2$$

which agrees with the given value of K .

See Exercise 13.46.

13.6 Solving Equilibrium Problems

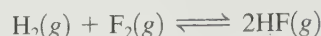
We have already considered most of the strategies needed to solve equilibrium problems. The typical procedure for analyzing a chemical equilibrium problem can be summarized as follows:

Procedure for Solving Equilibrium Problems

- ➡ **1** Write the balanced equation for the reaction.
- ➡ **2** Write the equilibrium expression using the law of mass action.
- ➡ **3** List the initial concentrations.
- ➡ **4** Calculate Q , and determine the direction of the shift to equilibrium.
- ➡ **5** Define the change needed to reach equilibrium, and define the equilibrium concentrations by applying the change to the initial concentrations.
- ➡ **6** Substitute the equilibrium concentrations into the equilibrium expression, and solve for the unknown.
- ➡ **7** Check your calculated equilibrium concentrations by making sure they give the correct value of K .

So far we have been careful to choose systems in which we can solve for the unknown by taking the square root of both sides of the equation. However, this type of system is not really very common, and we must now consider a more typical problem. Suppose for a synthesis of hydrogen fluoride from hydrogen and fluorine, 3.000 mol H_2 and 6.000 mol F_2 are mixed in a 3.000-L flask. Assume that the equilibrium constant for the synthesis reaction at this temperature is 1.15×10^2 . We calculate the equilibrium concentration of each component as follows:

➡ **1** We begin, as usual, by writing the balanced equation for the reaction:



➡ **2** The equilibrium expression is

$$K = 1.15 \times 10^2 = \frac{[\text{HF}]^2}{[\text{H}_2][\text{F}_2]}$$

➡ **3** The initial concentrations are

$$[\text{H}_2]_0 = \frac{3.000 \text{ mol}}{3.000 \text{ L}} = 1.000 \text{ M}$$

$$[\text{F}_2]_0 = \frac{6.000 \text{ mol}}{3.000 \text{ L}} = 2.000 \text{ M}$$

$$[\text{HF}]_0 = 0$$

➡ **4** There is no need to calculate Q because no HF is present initially, and we know that the system must shift to the right to reach equilibrium.

➡ **5** If we let x represent the number of moles per liter of H_2 consumed to reach equilibrium, we can represent the equilibrium concentrations as follows:

	$\text{H}_2(\text{g})$	+	$\text{F}_2(\text{g})$	$\rightleftharpoons$	$2\text{HF}(\text{g})$
Initial:	1.000		2.000		0
Change:	$-x$		$-x$		$+2x$
Equilibrium:	$1.000 - x$		$2.000 - x$		$2x$

➡ **6** Substituting the equilibrium concentrations into the equilibrium expression gives

$$K = 1.15 \times 10^2 = \frac{[\text{HF}]^2}{[\text{H}_2][\text{F}_2]} = \frac{(2x)^2}{(1.000 - x)(2.000 - x)}$$

Since the right side of this equation is not a perfect square, we cannot take the square root of both sides, but must use some other procedure.

First, do the indicated multiplication:

$$(1.000 - x)(2.000 - x)(1.15 \times 10^2) = (2x)^2$$

$$\text{or} \quad (1.15 \times 10^2)x^2 - 3.000(1.15 \times 10^2)x + 2.000(1.15 \times 10^2) = 4x^2$$

and collect terms

$$(1.11 \times 10^2)x^2 - (3.45 \times 10^2)x + 2.30 \times 10^2 = 0$$

This is a quadratic equation of the general form

$$ax^2 + bx + c = 0$$

Use of the quadratic formula is explained in Appendix 1.4.

where the roots can be obtained from the quadratic formula:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

In this example, $a = 1.11 \times 10^2$, $b = -3.45 \times 10^2$, and $c = 2.30 \times 10^2$. Substituting these values into the quadratic formula gives two values for x :

$$x = 2.14 \text{ mol/L} \quad \text{and} \quad x = 0.968 \text{ mol/L}$$

Both these results cannot be valid (since a *given* set of initial concentrations leads to only *one* equilibrium position). How can we choose between them? Since the expression for the equilibrium concentration of H_2 is

$$[\text{H}_2] = 1.000 \text{ M} - x$$

the value of x cannot be 2.14 mol/L (because subtracting 2.14 M from 1.000 M gives a negative concentration of H_2 , which is physically impossible). Thus the correct value for x is 0.968 mol/L, and the equilibrium concentrations are as follows:

$$[\text{H}_2] = 1.000 \text{ M} - 0.968 \text{ M} = 3.2 \times 10^{-2} \text{ M}$$

$$[\text{F}_2] = 2.000 \text{ M} - 0.968 \text{ M} = 1.032 \text{ M}$$

$$[\text{HF}] = 2(0.968 \text{ M}) = 1.936 \text{ M}$$

 **7** We can check these concentrations by substituting them into the equilibrium expression:

$$\frac{[\text{HF}]^2}{[\text{H}_2][\text{F}_2]} = \frac{(1.936)^2}{(3.2 \times 10^{-2})(1.032)} = 1.13 \times 10^2$$

This value is in close agreement with the given value for K (1.15×10^2), so the calculated equilibrium concentrations are correct.

This procedure is further illustrated for a problem involving pressures in Sample Exercise 13.12.

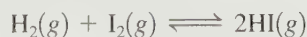
SAMPLE EXERCISE 13.12

Calculating Equilibrium Pressures

Assume that gaseous hydrogen iodide is synthesized from hydrogen gas and iodine vapor at a temperature where the equilibrium constant is 1.00×10^2 . Suppose HI at 5.000×10^{-1} atm, H_2 at 1.000×10^{-2} atm, and I_2 at 5.000×10^{-3} atm are mixed in a 5.000-L flask. Calculate the equilibrium pressures of all species.

SOLUTION

The balanced equation for this process is



and the equilibrium expression in terms of pressure is

$$K_p = \frac{P_{\text{HI}}^2}{(P_{\text{H}_2})(P_{\text{I}_2})} = 1.00 \times 10^2$$

The given initial pressures are

$$P_{\text{HI}}^0 = 5.000 \times 10^{-1} \text{ atm}$$

$$P_{\text{H}_2}^0 = 1.000 \times 10^{-2} \text{ atm}$$

$$P_{\text{I}_2}^0 = 5.000 \times 10^{-3} \text{ atm}$$

The value of Q for this system is

$$Q = \frac{(P_{\text{HI}}^0)^2}{(P_{\text{H}_2}^0)(P_{\text{I}_2}^0)} = \frac{(5.000 \times 10^{-1} \text{ atm})^2}{(1.000 \times 10^{-2} \text{ atm})(5.000 \times 10^{-3} \text{ atm})} = 5.000 \times 10^3$$

Since Q is greater than K , the system will shift to the left to reach equilibrium.

So far we have used moles or concentrations in stoichiometric calculations. However, it is equally valid to use pressures for a gas-phase system at constant temperature and volume because in this case pressure is directly proportional to the number of moles:

$$P = n \left(\frac{RT}{V} \right) \leftarrow \text{Constant if constant } T \text{ and } V$$

Thus we can represent the change needed to achieve equilibrium in terms of pressures.

Let x be the change in pressure (in atm) of H_2 as the system shifts left toward equilibrium. This leads to the following equilibrium pressures:

	$\text{H}_2(\text{g})$	+	$\text{I}_2(\text{g})$	$\rightleftharpoons$	$2\text{HI}(\text{g})$
Initial:	1.000×10^{-2}		5.000×10^{-3}		5.000×10^{-1}
Change:	$+x$		$+x$		$-2x$
Equilibrium:	$1.000 \times 10^{-2} + x$		$5.000 \times 10^{-3} + x$		$5.000 \times 10^{-1} - 2x$

Substitution into the equilibrium expression gives

$$K_p = \frac{(P_{\text{HI}})^2}{(P_{\text{H}_2})(P_{\text{I}_2})} = \frac{(5.000 \times 10^{-1} - 2x)^2}{(1.000 \times 10^{-2} + x)(5.000 \times 10^{-3} + x)}$$

Multiplying and collecting terms yield the quadratic equation where $a = 9.60 \times 10^1$, $b = 3.5$, and $c = -2.45 \times 10^{-1}$:

$$(9.60 \times 10^1)x^2 + 3.5x - (2.45 \times 10^{-1}) = 0$$

From the quadratic formula, the correct value for x is $x = 3.55 \times 10^{-2} \text{ atm}$. The equilibrium pressures can now be calculated from the expressions involving x :

$$P_{\text{HI}} = 5.000 \times 10^{-1} \text{ atm} - 2(3.55 \times 10^{-2}) \text{ atm} = 4.29 \times 10^{-1} \text{ atm}$$

$$P_{\text{H}_2} = 1.000 \times 10^{-2} \text{ atm} + 3.55 \times 10^{-2} \text{ atm} = 4.55 \times 10^{-2} \text{ atm}$$

$$P_{\text{I}_2} = 5.000 \times 10^{-3} \text{ atm} + 3.55 \times 10^{-2} \text{ atm} = 4.05 \times 10^{-2} \text{ atm}$$

CHECK:

$$\frac{P_{\text{HI}}^2}{P_{\text{H}_2} \cdot P_{\text{I}_2}} = \frac{(4.29 \times 10^{-1})^2}{(4.55 \times 10^{-2})(4.05 \times 10^{-2})} = 99.9$$

This agrees with the given value of K (1.00×10^2), so the calculated equilibrium concentrations are correct.

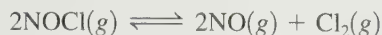
See Exercises 13.47 through 13.50.

Treating Systems That Have Small Equilibrium Constants

We have seen that fairly complicated calculations are often necessary to solve equilibrium problems. However, under certain conditions, simplifications are possible that greatly reduce the mathematical difficulties. For example, gaseous NOCl de-

composes to form the gases NO and Cl₂. At 35°C the equilibrium constant is 1.6×10^{-5} . In an experiment in which 1.0 mol NOCl is placed in a 2.0-L flask, what are the equilibrium concentrations?

The balanced equation is

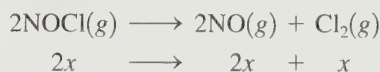


and
$$K = \frac{[\text{NO}]^2[\text{Cl}_2]}{[\text{NOCl}]^2} = 1.6 \times 10^{-5}$$

The initial concentrations are

$$[\text{NOCl}]_0 = \frac{1.0 \text{ mol}}{2.0 \text{ L}} = 0.50 \text{ M} \quad [\text{NO}]_0 = 0 \quad [\text{Cl}_2]_0 = 0$$

Since there are no products initially, the system will move to the right to reach equilibrium. We will define x as the change in concentration of Cl₂ needed to reach equilibrium. The changes in the concentrations of NOCl and NO can then be obtained from the balanced equation:



The concentrations can be summarized as follows:

	2NOCl(g)	$\rightleftharpoons$	2NO(g)	+	Cl ₂ (g)
Initial:	0.50		0		0
Change:	-2x		+2x		+x
Equilibrium:	0.50 - 2x		2x		x

The equilibrium concentrations must satisfy the equilibrium expression

$$K = 1.6 \times 10^{-5} = \frac{[\text{NO}]^2[\text{Cl}_2]}{[\text{NOCl}]^2} = \frac{(2x)^2(x)}{(0.50 - 2x)^2}$$

Multiplying and collecting terms will give an equation with terms containing x^3 , x^2 , and x , which requires complicated methods to solve directly. However, we can avoid this situation by recognizing that since K is so small (1.6×10^{-5}), the system will not proceed far to the right to reach equilibrium. That is, x represents a relatively small number. The consequence of this fact is that the term $(0.50 - 2x)$ can be approximated by 0.50. That is, when x is small,

$$0.50 - 2x \approx 0.50$$

Making this approximation allows us to simplify the equilibrium expression:

$$1.6 \times 10^{-5} = \frac{(2x)^2(x)}{(0.50 - 2x)^2} \approx \frac{(2x)^2(x)}{(0.50)^2} = \frac{4x^3}{(0.50)^2}$$

Solving for x^3 gives

$$x^3 = \frac{(1.6 \times 10^{-5})(0.50)^2}{4} = 1.0 \times 10^{-6}$$

and $x = 1.0 \times 10^{-2}$.

How valid is this approximation? If $x = 1.0 \times 10^{-2}$, then

$$0.50 - 2x = 0.50 - 2(1.0 \times 10^{-2}) = 0.48$$

Approximations can simplify complicated math, but their validity should be checked carefully.

The difference between 0.50 and 0.48 is 0.02, or 4% of the initial concentration of NOCl, a relatively small discrepancy that will have little effect on the outcome. That is, since $2x$ is very small compared with 0.50, the value of x obtained in the approximate solution should be very close to the exact value. We use this approximate value of x to calculate the equilibrium concentrations:

$$\begin{aligned}[\text{NOCl}] &= 0.50 - 2x \approx 0.50 \text{ M} \\[\text{NO}] &= 2x = 2(1.0 \times 10^{-2} \text{ M}) = 2.0 \times 10^{-2} \text{ M} \\[\text{Cl}_2] &= x = 1.0 \times 10^{-2} \text{ M}\end{aligned}$$

CHECK:

$$\frac{[\text{NO}]^2[\text{Cl}_2]}{[\text{NOCl}]^2} = \frac{(2.0 \times 10^{-2})^2(1.0 \times 10^{-2})}{(0.50)^2} = 1.6 \times 10^{-5}$$

Since the given value of K is 1.6×10^{-5} , these calculated concentrations are correct.

This problem was much easier to solve than it appeared at first because the *small value of K and the resulting small shift to the right to reach equilibrium allowed simplification.*

13.7 Le Châtelier's Principle

It is important to understand the factors that control the *position* of a chemical equilibrium. For example, when a chemical is manufactured, the chemists and chemical engineers in charge of production want to choose conditions that favor the desired product as much as possible. That is, they want the equilibrium to lie far to the right. When Fritz Haber was developing the process for the synthesis of ammonia, he did extensive studies on how temperature and pressure affect the equilibrium concentration of ammonia. Some of his results are given in Table 13.2. Note that the equilibrium amount of NH_3 increases with an increase in pressure but decreases as the temperature is increased. Thus the amount of NH_3 present at equilibrium is favored by conditions of low temperature and high pressure.

However, this is not the whole story. Carrying out the process at low temperatures is not feasible because then the reaction is too slow. Even though the equilibrium tends to shift to the right as the temperature is lowered, the attainment of equilibrium would be much too slow at low temperatures to be practical. This emphasizes once again that we must study both the thermodynamics and the kinetics of a reaction before we really understand the factors that control it.

We can qualitatively predict the effects of changes in concentration, pressure, and temperature on a system at equilibrium by using **Le Châtelier's principle**,

TABLE 13.2 The Percent by Mass of NH_3 at Equilibrium in a Mixture of N_2 , H_2 , and NH_3 as a Function of Temperature and Total Pressure*

Temperature (°C)	Total Pressure		
	300 atm	400 atm	500 atm
400	48% NH_3	55% NH_3	61% NH_3
500	26% NH_3	32% NH_3	38% NH_3
600	13% NH_3	17% NH_3	21% NH_3

*Each experiment was begun with a 3:1 mixture of H_2 and N_2 .

which states that *if a change is imposed on a system at equilibrium, the position of the equilibrium will shift in a direction that tends to reduce that change*. Although this rule sometimes oversimplifies the situation, it works remarkably well.

The Effect of a Change in Concentration

To see how we can predict the effect of change in concentration on a system at equilibrium, we will consider the ammonia synthesis reaction. Suppose there is an equilibrium position described by these concentrations:

$$[\text{N}_2] = 0.399 \text{ M} \quad [\text{H}_2] = 1.197 \text{ M} \quad [\text{NH}_3] = 0.202 \text{ M}$$

What will happen if 1.000 mol/L N_2 is suddenly injected into the system? We can answer this question by calculating the value of Q . The concentrations before the system adjusts are

$$\begin{aligned} [\text{N}_2]_0 &= 0.399 \text{ M} + 1.000 \text{ M} = 1.399 \text{ M} \\ &\quad \uparrow \\ &\quad \text{Added N}_2 \\ [\text{H}_2]_0 &= 1.197 \text{ M} \\ [\text{NH}_3]_0 &= 0.202 \text{ M} \end{aligned}$$

Note we are labeling these as “initial concentrations” because the system is no longer at equilibrium. Then

$$Q = \frac{[\text{NH}_3]_0^2}{[\text{N}_2]_0[\text{H}_2]_0^3} = \frac{(0.202)^2}{(1.399)(1.197)^3} = 1.70 \times 10^{-2}$$

Since we are not given the value of K , we must calculate it from the first set of equilibrium concentrations:

$$K = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(0.202)^2}{(0.399)(1.197)^3} = 5.96 \times 10^{-2}$$

As expected, Q is less than K because the concentration of N_2 was increased.

The system will shift to the right to come to the new equilibrium position. Rather than do the calculations, we simply summarize the results:

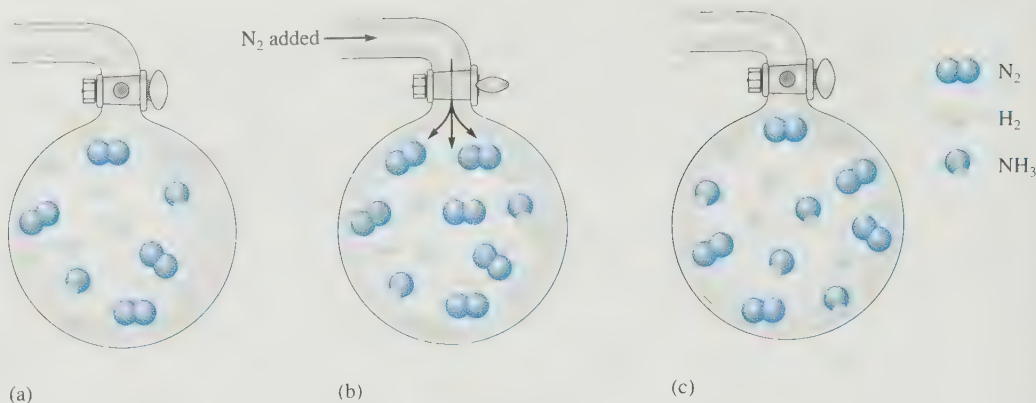
Equilibrium Position I		Equilibrium Position II
$[\text{N}_2] = 0.399 \text{ M}$	$\xrightarrow[\text{of N}_2 \text{ added}]{1.000 \text{ mol/L}}$	$[\text{N}_2] = 1.348 \text{ M}$
$[\text{H}_2] = 1.197 \text{ M}$		$[\text{H}_2] = 1.044 \text{ M}$
$[\text{NH}_3] = 0.202 \text{ M}$		$[\text{NH}_3] = 0.304 \text{ M}$

Note from these data that the equilibrium position does in fact shift to the right: The concentration of H_2 decreases, the concentration of NH_3 increases, and of course, since nitrogen is added, the concentration of N_2 shows an increase relative to the amount present in the original equilibrium position. (However, notice that the nitrogen showed a decrease relative to the amount present immediately after addition of the 1.000 mol N_2 .)

We can understand this shift by thinking about reaction rates. When we add N_2 molecules to the system, the number of collisions between N_2 and H_2 will increase, thus increasing the rate of the forward reaction and in turn increasing the rate of formation of NH_3 molecules. More NH_3 molecules will in turn lead to a higher rate for the reverse reaction. Eventually, the forward and reverse reaction rates will again become equal, and the system will reach its new equilibrium position.

FIGURE 13.8

(a) The initial equilibrium mixture of N_2 , H_2 , and NH_3 . (b) Addition of N_2 . (c) The new equilibrium position for the system containing more N_2 (due to addition of N_2), less H_2 , and more NH_3 than in (a).



We can predict this shift qualitatively by using Le Châtelier's principle. Since the change imposed is the addition of nitrogen, Le Châtelier's principle predicts that the system will shift in a direction that consumes nitrogen. This reduces the effect of the addition. Thus Le Châtelier's principle correctly predicts that adding nitrogen will cause the equilibrium to shift to the right (see Fig. 13.8).

If ammonia had been added instead of nitrogen, the system would have shifted to the left to consume ammonia. So another way of stating Le Châtelier's principle is to say that *if a component (reactant or product) is added to a reaction system at equilibrium (at constant T and P or constant T and V), the equilibrium position will shift in the direction that lowers the concentration of that component. If a component is removed, the opposite effect occurs.*

The system shifts in the direction that compensates for the imposed change.

SAMPLE EXERCISE 13.13

Using Le Châtelier's Principle I

Arsenic can be extracted from its ores by first reacting the ore with oxygen (called *roasting*) to form solid As_4O_6 , which is then reduced using carbon:



Predict the direction of the shift of the equilibrium position in response to each of the following changes in conditions.

- Addition of carbon monoxide
- Addition or removal of carbon or tetraarsenic hexoxide (As_4O_6)
- Removal of gaseous arsenic (As_4)

SOLUTION

- Le Châtelier's principle predicts that the shift will be away from the substance whose concentration is increased. The equilibrium position will shift to the left when carbon monoxide is added.
- Since the amount of a pure solid has no effect on the equilibrium position, changing the amount of carbon or tetraarsenic hexoxide will have no effect.
- If gaseous arsenic is removed, the equilibrium position will shift to the right to form more products. In industrial processes, the desired product is often continuously removed from the reaction system to increase the yield.

See Exercise 13.57.

The Effect of a Change in Pressure

Basically, there are three ways to change the pressure of a reaction system involving gaseous components:

1. Add or remove a gaseous reactant or product.
2. Add an inert gas (one not involved in the reaction).
3. Change the volume of the container.

We have already considered the addition or removal of a reactant or product. When an inert gas is added, there is no effect on the equilibrium position. *The addition of an inert gas increases the total pressure but has no effect on the concentrations or partial pressures of the reactants or products.* That is, in this case the added molecules do not participate in the reaction in any way and thus cannot affect the equilibrium in any way. Thus the system remains at the original equilibrium position.

When the volume of the container is changed, the concentrations (and thus the partial pressures) of both reactants and products are changed. We could calculate Q and predict the direction of the shift. However, for systems involving gaseous components, there is an easier way: We focus on the volume. The central idea is that *when the volume of the container holding a gaseous system is reduced, the system responds by reducing its own volume. This is done by decreasing the total number of gaseous molecules in the system.*

To see that this is true, we can rearrange the ideal gas law to give

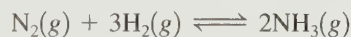
$$V = \left(\frac{RT}{P} \right) n$$

or at constant T and P ,

$$V \propto n$$

That is, at constant temperature and pressure, the volume of a gas is directly proportional to the number of moles of gas present.

Suppose we have a mixture of the gases nitrogen, hydrogen, and ammonia at equilibrium (Fig. 13.9). If we suddenly reduce the volume, what will happen to the equilibrium position? The reaction system can reduce its volume by reducing the number of molecules present. This means that the reaction



will shift to the right, since in this direction four molecules (one of nitrogen and three of hydrogen) react to produce two molecules (of ammonia), thus *reducing the total number of gaseous molecules present.* The new equilibrium position will be

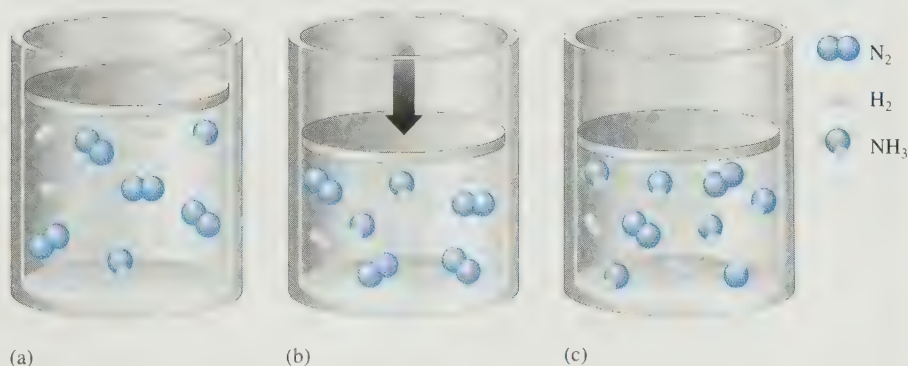


FIGURE 13.9

(a) A mixture of $\text{NH}_3(\text{g})$, $\text{N}_2(\text{g})$, and $\text{H}_2(\text{g})$ at equilibrium. (b) The volume is suddenly decreased. (c) The new equilibrium position for the system containing more NH_3 and less N_2 and H_2 . The reaction $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ shifts to the right (toward the side with fewer molecules) when the container volume is decreased.

farther to the right than the original one. That is, the equilibrium position will shift toward the side of the reaction involving the smaller number of gaseous molecules in the balanced equation.

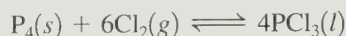
The opposite is also true. When the container volume is increased, the system will shift so as to increase its volume. An increase in volume in the ammonia synthesis system will produce a shift to the left to increase the total number of gaseous molecules present.

SAMPLE EXERCISE 13.14

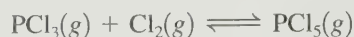
Using Le Châtelier's Principle II

Predict the shift in equilibrium position that will occur for each of the following processes when the volume is reduced.

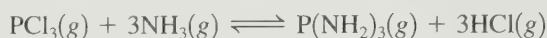
- a. The preparation of liquid phosphorus trichloride by the reaction



- b. The preparation of gaseous phosphorus pentachloride according to the equation



- c. The reaction of phosphorus trichloride with ammonia:



SOLUTION

- a. Since P_4 and PCl_3 are a pure solid and a pure liquid, respectively, we need to consider only the effect of the change in volume on Cl_2 . The volume is decreased, so the position of the equilibrium will shift to the right, since the reactant side contains six gaseous molecules and the product side has none.
- b. Decreasing the volume will shift the given reaction to the right, since the product side contains only one gaseous molecule while the reactant side has two.

(a) Brown $\text{NO}_2(g)$ and colorless $\text{N}_2\text{O}_4(g)$ in equilibrium in a syringe.
 (b) The volume is suddenly decreased, giving a greater concentration of both N_2O_4 and NO_2 (indicated by the darker brown color).
 (c) A few seconds after the sudden volume decrease, the color is much lighter brown as the equilibrium shifts the brown $\text{NO}_2(g)$ to colorless $\text{N}_2\text{O}_4(g)$ as predicted by Le Châtelier's principle, since in the equilibrium



the product side has the smaller number of molecules.



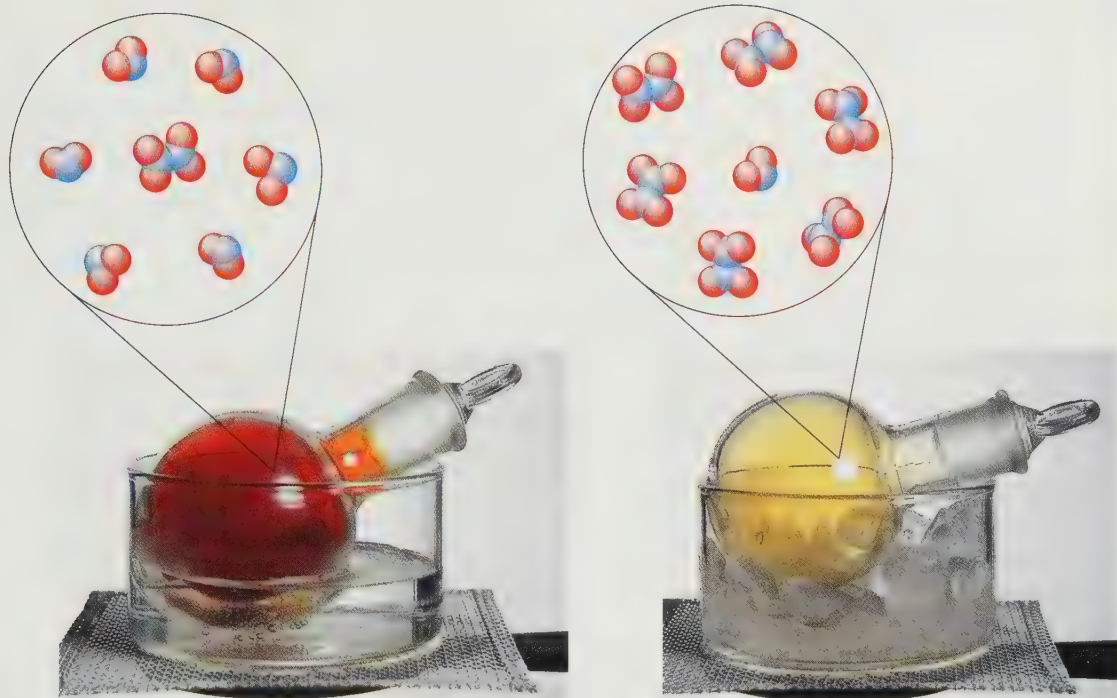
(a)



(b)



(c)



Shifting the $\text{N}_2\text{O}_4(g) \rightarrow 2\text{NO}_2(g)$ equilibrium by changing the temperature. (a) At 100°C the flask is definitely reddish brown due to a large amount of NO_2 present. (b) At 0°C the equilibrium is shifted toward colorless $\text{N}_2\text{O}_4(g)$.

- c. Both sides of the balanced reaction equation have four gaseous molecules. A change in volume will have no effect on the equilibrium position. There is no shift in this case.

See Exercise 13.58.

The Effect of a Change in Temperature

It is important to realize that although the changes we have just discussed may alter the equilibrium *position*, they do not alter the equilibrium *constant*. For example, the addition of a reactant shifts the equilibrium position to the right but has no effect on the value of the equilibrium constant; the new equilibrium concentrations satisfy the original equilibrium constant.

The effect of temperature on equilibrium is different, however, because *the value of K changes with temperature*. We can use Le Châtelier's principle to predict the direction of the change.

The synthesis of ammonia from nitrogen and hydrogen is exothermic. We can represent this by treating energy as a product:



If energy is added to this system at equilibrium by heating it, Le Châtelier's principle predicts that the shift will be in the direction that consumes energy, that is, to the left. Note that this shift decreases the concentration of NH_3 and increases the concentrations of N_2 and H_2 , thus *decreasing the value of K* . The experimentally observed change in K with temperature for this reaction is indicated in Table 13.3. The value of K decreases with increased temperature, as predicted.

On the other hand, for an endothermic reaction, such as the decomposition of calcium carbonate,



Of course, energy is not a chemical product of this reaction, but thinking of it in this way makes it easy to apply Le Châtelier's principle.

an increase in temperature will cause the equilibrium to shift to the right and the value of K to increase.

In summary, to use Le Châtelier's principle to describe the effect of a temperature change on a system at equilibrium, treat energy as a reactant (in an endothermic process) or as a product (in an exothermic process), and predict the direction of the shift in the same way as when an actual reactant or product is added or removed. Although Le Châtelier's principle cannot predict the size of the change in K , it does correctly predict the direction of the change.

SAMPLE EXERCISE 13.15

Using Le Châtelier's Principle III

For each of the following reactions, predict how the value of K changes as the temperature is increased.

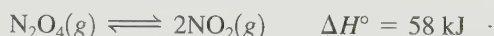
- a. $\text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}(g) \quad \Delta H^\circ = 181 \text{ kJ}$
 b. $2\text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{SO}_3(g) \quad \Delta H^\circ = -198 \text{ kJ}$

SOLUTION

- a. This is an endothermic reaction, as indicated by the positive value for ΔH° . Energy can be viewed as a reactant, and K increases (the equilibrium shifts to the right) as the temperature is increased.
 b. This is an exothermic reaction (energy can be regarded as a product). As the temperature is increased, the value of K decreases (the equilibrium shifts to the left).

See Exercises 13.59 through 13.64.

We have seen how Le Châtelier's principle can be used to predict the effect of several types of changes on a system at equilibrium. To summarize these ideas, Table 13.4 shows how various changes affect the equilibrium position of the endothermic reaction



For Review

Summary

For stoichiometry calculations, we assume that reactions run to completion. However, when a chemical reaction is carried out in a closed vessel, the system achieves chemical equilibrium, the state where the concentrations of both reactants and products remain constant over time. Although a particular equilibrium concentration may be small, it is never zero. Equilibrium is a highly dynamic state; reactants are converted continually to products, and vice versa, as molecules collide with each other. At equilibrium the rates of the forward and reverse reactions are equal.

The law of mass action is a general description of the equilibrium condition. It states that for a reaction of the type



TABLE 13.3

Observed Value of K for the Ammonia Synthesis Reaction as a Function of Temperature*

Temperature (K)	K
500	90
600	3
700	0.3
800	0.04

*For this exothermic reaction, the value of K decreases as the temperature increases, as predicted by Le Châtelier's principle.

TABLE 13.4 Shifts in the Equilibrium Position for the Reaction $58 \text{ kJ} + \text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$

Change	Shift
Addition of $\text{N}_2\text{O}_4(g)$	Right
Addition of $\text{NO}_2(g)$	Left
Removal of $\text{N}_2\text{O}_4(g)$	Left
Removal of $\text{NO}_2(g)$	Right
Addition of $\text{He}(g)$	None
Decrease container volume	Left
Increase container volume	Right
Increase temperature	Right
Decrease temperature	Left

Key Terms

chemical equilibrium

Section 13.2

law of mass action

equilibrium expression

equilibrium constant

equilibrium position

Section 13.4

homogeneous equilibria

heterogeneous equilibria

Section 13.5

reaction quotient Q

Section 13.7

Le Châtelier's principle

the equilibrium expression is given by

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

where K is the equilibrium constant.

For each reaction system at a given temperature, there is only one value for the equilibrium constant but an infinite number of possible equilibrium positions. An equilibrium position is defined by a particular set of concentrations (equilibrium concentrations) that satisfies the equilibrium expression. The specific equilibrium position attained by a system depends on the initial concentrations. An equilibrium position never depends on the amount of a pure liquid or a pure solid, and therefore, these substances are not included in the equilibrium expression.

For a gas-phase reaction, equilibrium positions also can be described in terms of partial pressures. K_p , the equilibrium constant in terms of pressures, is related to K as follows:

$$K_p = K(RT)^{\Delta n}$$

where Δn is the sum of the coefficients of the gaseous products minus the sum of the coefficients of the gaseous reactants.

Homogeneous equilibria involve reactions where all reactants and products are in the same phase. However, many systems involve different phases, and their equilibria are described as heterogeneous.

The value of K allows us to predict the inherent tendency of a reaction to occur. A small value of K means that the equilibrium position lies far to the left, and therefore the reaction will not occur to any great extent. A large value of K means that the reaction will go essentially to completion—the equilibrium position lies far to the right. However, the value of K gives no information concerning how rapidly equilibrium will be achieved.

The reaction quotient Q applies the law of mass action to initial rather than equilibrium concentrations. We compare Q to K to determine in which direction a chemical system will shift to reach equilibrium. If Q is equal to K , the system is already at equilibrium; if Q is less than K , the system will shift to the right to reach equilibrium; if Q is greater than K , the system will shift to the left to reach equilibrium.

To find the concentrations that characterize a given equilibrium position, it is usually best to start with the given initial concentrations (or pressures), define the change needed to reach equilibrium, and apply this change to the initial concentrations (or pressures) to define the equilibrium concentrations (or pressures).

Le Châtelier's principle allows us to predict qualitatively the effects of changes in concentration, pressure, and temperature on a system at equilibrium. This principle states that if a change is imposed, the equilibrium position will shift in a direction that tends to compensate for the imposed change.

In-Class Discussion Questions

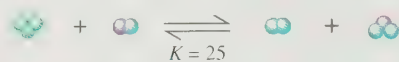
These questions are designed to be considered by groups of students in class. Often these questions work well for introducing a particular topic in class.

1. Consider an equilibrium mixture of four chemicals (A, B, C, and D, all gases) reacting in a closed flask according to the equation:

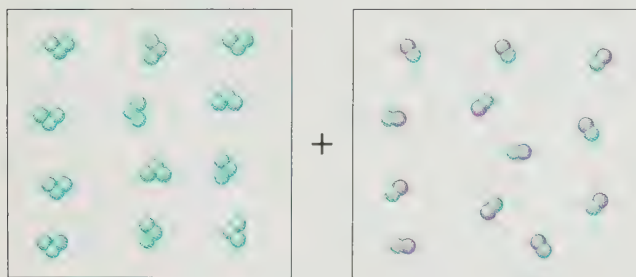


- a. You add more A to the flask. How does the concentration of each chemical compare to its original concentration after equilibrium is reestablished? Justify your answer.
- b. You have the original setup at equilibrium, and add more D to the flask. How does the concentration of each chemical compare to its original concentration after equilibrium is reestablished? Justify your answer.

2. The boxes shown below represent a set of initial conditions for the reaction:



Draw a quantitative molecular picture that shows what this system looks like after the reactants are mixed in one of the boxes and the system reaches equilibrium. Support your answer with calculations.



3. For the reaction, $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$, consider two possibilities: (a) you mix 0.5 mol of each reactant, allow the system to come to equilibrium, and then add another mole of H_2 and allow the system to reach equilibrium again, or (b) you mix 1.5 mol H_2 and 0.5 mol I_2 and allow the system to reach equilibrium. Will the final equilibrium mixture be different for the two procedures? Explain.

4. Given the reaction, $\text{A}(\text{g}) + \text{B}(\text{g}) \rightleftharpoons \text{C}(\text{g}) + \text{D}(\text{g})$, consider the following situations:

- You have 1.3 M A and 0.8 M B initially.
- You have 1.3 M A, 0.8 M B, and 0.2 M C initially.
- You have 2.0 M A and 0.8 M B initially.

Order the preceding situations in terms of increasing equilibrium concentration of D. Explain your order. Then give the order in terms of increasing equilibrium concentration of B and explain.

5. Consider the reaction $\text{A}(\text{g}) + 2\text{B}(\text{g}) \rightleftharpoons \text{C}(\text{g}) + \text{D}(\text{g})$ in a 1.0-L rigid flask. Answer the following questions for each situation (a–d):

- Estimate a range (as small as possible) for the requested substance. For example, [A] could be between 95 M and 100 M.
 - Explain how you decided on the limits for the estimated range.
 - Indicate what other information would enable you to narrow your estimated range.
 - Compare the estimated concentrations for a through d, and explain any differences.
- If at equilibrium [A] = 1 M, and then 1 mol C is added, estimate the value for [A] once equilibrium is reestablished.
 - If at equilibrium [B] = 1 M, and then 1 mol C is added, estimate the value for [B] once equilibrium is reestablished.
 - If at equilibrium [C] = 1 M, and then 1 mol C is added, estimate the value for [C] once equilibrium is reestablished.

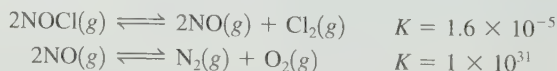
- If at equilibrium [D] = 1 M, and then 1 mol C is added, estimate the value for [D] once equilibrium is reestablished.

6. Consider the reaction $\text{A}(\text{g}) + \text{B}(\text{g}) \rightleftharpoons \text{C}(\text{g}) + \text{D}(\text{g})$. A friend asks the following: “I know we have been told that if a mixture of A, B, C, and D is at equilibrium and more of A is added, more C and D will form. But how can more C and D form if we do not add more B?” What do you tell your friend?
7. Consider the following statements: “Consider the reaction $\text{A}(\text{g}) + \text{B}(\text{g}) \rightleftharpoons \text{C}(\text{g})$, for which at equilibrium [A] = 2 M, [B] = 1 M, and [C] = 4 M. To a 1-L container of the system at equilibrium you add 3 moles of B. A possible equilibrium condition is [A] = 1 M, [B] = 3 M, and [C] = 6 M because in both cases $K = 2$.” Indicate everything that is correct in these statements and everything that is incorrect. Correct the incorrect statements, and explain.
8. Le Châtelier’s principle is stated (Section 13.7) as follows: “If a change is imposed on a system at equilibrium, the position of the equilibrium will shift in a direction that tends to reduce that change.” The system $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$ is used as an example in which the addition of nitrogen gas at equilibrium results in a decrease in H_2 concentration and an increase in NH_3 concentration. In the experiment the volume is assumed to be constant. On the other hand, if N_2 is added to the reaction system in a container with a piston so that the pressure can be held constant, the amount of NH_3 actually could decrease and the concentration of H_2 would increase as equilibrium is reestablished. Explain how this can happen. Also, if you consider this same system at equilibrium, the addition of an inert gas, holding the pressure constant, *does* affect the equilibrium position. Explain why the addition of an inert gas to this system in a rigid container does not affect the equilibrium position.

A blue question or exercise number indicates that the answer to that question or exercise appears at the back of this book and a solution appears in the *Solutions Guide*.

Questions

- Characterize a system at chemical equilibrium with respect to each of the following.
 - the rates of the forward and reverse reactions
 - the overall composition of the reaction mixture
- Is the following statement true or false? “Reactions with large equilibrium constants are very fast.” Explain.
- There is only one value of the equilibrium constant for a particular system at a particular temperature, but there is an infinite number of equilibrium positions. Explain.
- Consider the following reactions at some temperature:



For each reaction some quantities of the reactants were placed in separate containers and allowed to come to equilibrium.

Describe the relative amounts of reactants and products that are present at equilibrium. At equilibrium, which is faster, the forward or reverse reaction in each case?

13. Distinguish between the terms *equilibrium constant* and *reaction quotient*.
14. How will the equilibrium position of a gas-phase reaction be affected if the volume of the reaction vessel changes? Are there reactions that will not have their equilibria shifted by a change in volume? Explain. Why does changing the pressure in a rigid container by adding an inert gas not shift the equilibrium position for a gas-phase reaction?

Exercises

In this section similar exercises are paired.

Characteristics of Chemical Equilibria

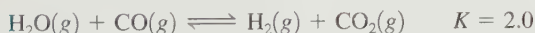
15. Consider the following reaction:



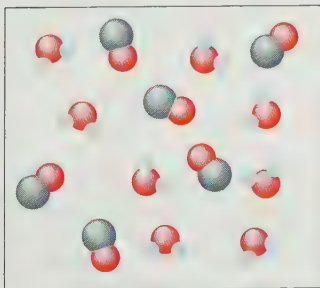
Amounts of H_2O , CO , H_2 , and CO_2 are put into a flask so that the composition corresponds to an equilibrium position. If the CO placed in the flask is labeled with radioactive ^{14}C , will ^{14}C be found only in CO molecules for an indefinite period of time? Explain.

16. Consider the same reaction as in Exercise 15. In one experiment 1.0 mol $\text{H}_2\text{O}(g)$ and 1.0 mol $\text{CO}(g)$ are put into a flask and heated to 350°C . In a second experiment 1.0 mol $\text{H}_2(g)$ and 1.0 mol $\text{CO}_2(g)$ are put into another flask with the same volume as the first. This mixture is also heated to 350°C . After equilibrium is reached, will there be any difference in the composition of the mixtures in the two flasks?

17. Consider the following reaction at some temperature:

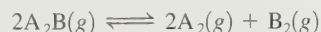


Some molecules of H_2O and CO are placed in a 1.0-L container as shown below.

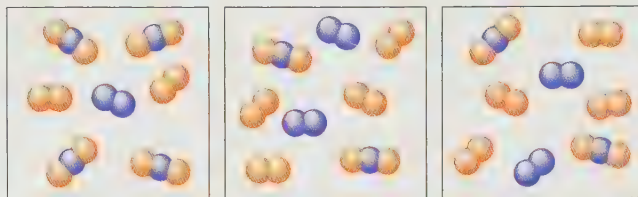


When equilibrium is reached, how many molecules of H_2O , CO , H_2 and CO_2 are present? Do this problem by trial and error—that is, if two molecules of CO react, is this equilibrium; if three molecules of CO react, is this equilibrium; and so on.

18. Consider the following generic reaction:



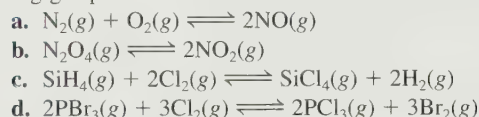
Some molecules of A_2B are placed in a 1.0-L container. As time passes, several snapshots of the reaction mixture are taken as illustrated below.



Which illustration is the first to represent an equilibrium mixture? Explain. How many molecules of A_2B reacted initially?

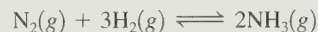
The Equilibrium Constant

19. Write the equilibrium expression (K) for each of the following gas-phase reactions.

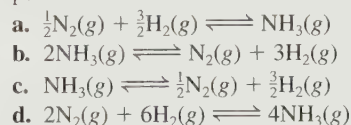


20. Write the equilibrium expression (K_p) for each reaction in Exercise 19.

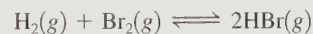
21. At a given temperature, $K = 1.3 \times 10^{-2}$ for the reaction



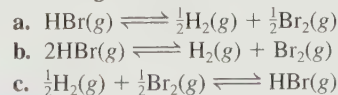
Calculate values of K for the following reactions at this temperature.



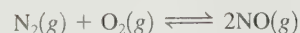
22. For the reaction



$K_p = 3.5 \times 10^4$ at 1495 K. What is the value of K_p for the following reactions at 1495 K?

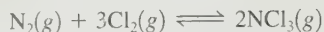


23. At high temperatures, elemental nitrogen and oxygen react with each other to form nitrogen monoxide:



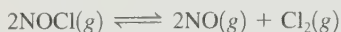
Suppose the system is analyzed at a particular temperature, and the equilibrium concentrations are found to be $[\text{N}_2] = 0.041\text{ M}$, $[\text{O}_2] = 0.0078\text{ M}$, and $[\text{NO}] = 4.7 \times 10^{-4}\text{ M}$. Calculate the value of K for the reaction.

24. For the reaction

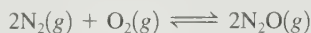


an analysis of an equilibrium mixture is performed at a certain temperature. It is found that $[\text{NCl}_3(\text{g})] = 1.9 \times 10^{-1} \text{ M}$, $[\text{N}_2(\text{g})] = 1.4 \times 10^{-3} \text{ M}$, and $[\text{Cl}_2(\text{g})] = 4.3 \times 10^{-4} \text{ M}$. Calculate K for the reaction at this temperature.

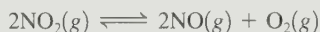
25. At a particular temperature, a 3.0-L flask contains 2.4 mol Cl_2 , 1.0 mol NOCl , and 4.5×10^{-3} mol NO . Calculate K at this temperature for the following reaction:



26. At a particular temperature a 2.00-L flask at equilibrium contains 2.80×10^{-4} mol N_2 , 2.50×10^{-5} mol O_2 , and 2.00×10^{-2} mol N_2O . Calculate K at this temperature for the reaction



27. The following equilibrium pressures at a certain temperature were observed for the reaction



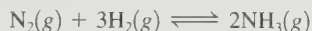
$$P_{\text{NO}_2} = 0.55 \text{ atm}$$

$$P_{\text{NO}} = 6.5 \times 10^{-5} \text{ atm}$$

$$P_{\text{O}_2} = 4.5 \times 10^{-5} \text{ atm}$$

Calculate the value for the equilibrium constant K_p at this temperature.

28. The following equilibrium pressures were observed at a certain temperature for the reaction



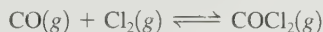
$$P_{\text{NH}_3} = 3.1 \times 10^{-2} \text{ atm}$$

$$P_{\text{N}_2} = 8.5 \times 10^{-1} \text{ atm}$$

$$P_{\text{H}_2} = 3.1 \times 10^{-3} \text{ atm}$$

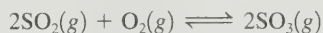
Calculate the value for the equilibrium constant K_p at this temperature.

29. At 25°C , $K = 3.7 \times 10^9$ for the reaction



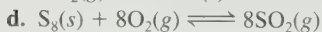
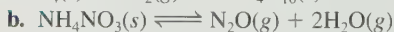
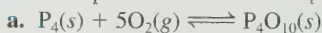
Calculate K_p at this temperature.

30. At 1100 K , $K_p = 0.25$ for the reaction



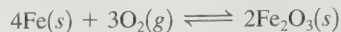
What is the value of K at this temperature?

31. Write expressions for K and K_p for the following reactions.



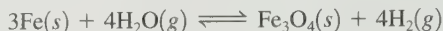
32. For which reactions in Exercise 31 is K_p equal to K ?

33. Consider the following reaction at a certain temperature:



An equilibrium mixture contains 1.0 mol Fe , 1.0×10^{-3} mol O_2 , and 2.0 mol Fe_2O_3 all in a 2.0-L container. Calculate the value of K for this reaction.

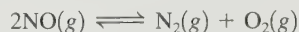
34. In a study of the reaction



at 1200 K it was observed that when the equilibrium partial pressure of water vapor is 15.0 torr , that total pressure at equilibrium is 36.3 torr . Calculate the value of K_p for this reaction at 1200 K . *Hint:* Apply Dalton's law of partial pressures.

Equilibrium Calculations

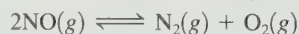
35. The equilibrium constant, K , is 2.4×10^3 at a certain temperature for the reaction



For which of the following sets of conditions is the system at equilibrium? For those that are not at equilibrium, in which direction will the system shift?

- A 1.0-L flask contains 0.024 mol NO , 2.0 mol N_2 , and 2.6 mol O_2 .
- A 2.0-L flask contains 0.032 mol NO , 0.62 mol N_2 , and 4.0 mol O_2 .
- A 3.0-L flask contains 0.060 mol NO , 2.4 mol N_2 , and 1.7 mol O_2 .

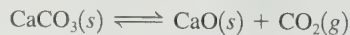
36. The equilibrium constant, K_p , is 2.4×10^3 at a certain temperature for the reaction



For which of the following sets of conditions is the system at equilibrium? For those that are not at equilibrium, in which direction will the system shift?

- $P_{\text{NO}} = 0.010 \text{ atm}$, $P_{\text{N}_2} = 0.11 \text{ atm}$, $P_{\text{O}_2} = 2.0 \text{ atm}$
- $P_{\text{NO}} = 0.0078 \text{ atm}$, $P_{\text{N}_2} = 0.36 \text{ atm}$, $P_{\text{O}_2} = 0.67 \text{ atm}$
- $P_{\text{NO}} = 0.0062 \text{ atm}$, $P_{\text{N}_2} = 0.51 \text{ atm}$, $P_{\text{O}_2} = 0.18 \text{ atm}$

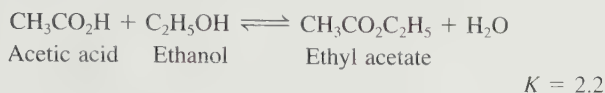
37. At 900°C , $K_p = 1.04$ for the reaction



At a low temperature, dry ice (solid CO_2), calcium oxide, and calcium carbonate are introduced into a 50.0-L reaction chamber. The temperature is raised to 900°C , resulting in the dry ice converting to gaseous CO_2 . For the following mixtures, will the initial amount of calcium oxide increase, decrease, or remain the same as the system moves toward equilibrium at 900°C ?

- 655 g CaCO_3 , 95.0 g CaO , $P_{\text{CO}_2} = 2.55 \text{ atm}$
- 780 g CaCO_3 , 1.00 g CaO , $P_{\text{CO}_2} = 1.04 \text{ atm}$
- 0.14 g CaCO_3 , 5000 g CaO , $P_{\text{CO}_2} = 1.04 \text{ atm}$
- 715 g CaCO_3 , 813 g CaO , $P_{\text{CO}_2} = 0.211 \text{ atm}$

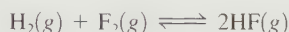
38. Ethyl acetate is synthesized in a nonreacting solvent (not water) according to the following reaction:



For the following mixtures (a–d), will the concentration of H_2O increase, decrease, or remain the same as equilibrium is established?

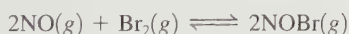
- $[\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5] = 0.22 \text{ M}$, $[\text{H}_2\text{O}] = 0.10 \text{ M}$, $[\text{CH}_3\text{CO}_2\text{H}] = 0.010 \text{ M}$, $[\text{C}_2\text{H}_5\text{OH}] = 0.010 \text{ M}$
- $[\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5] = 0.22 \text{ M}$, $[\text{H}_2\text{O}] = 0.0020 \text{ M}$, $[\text{CH}_3\text{CO}_2\text{H}] = 0.0020 \text{ M}$, $[\text{C}_2\text{H}_5\text{OH}] = 0.10 \text{ M}$
- $[\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5] = 0.88 \text{ M}$, $[\text{H}_2\text{O}] = 0.12 \text{ M}$, $[\text{CH}_3\text{CO}_2\text{H}] = 0.044 \text{ M}$, $[\text{C}_2\text{H}_5\text{OH}] = 6.0 \text{ M}$
- $[\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5] = 4.4 \text{ M}$, $[\text{H}_2\text{O}] = 4.4 \text{ M}$, $[\text{CH}_3\text{CO}_2\text{H}] = 0.88 \text{ M}$, $[\text{C}_2\text{H}_5\text{OH}] = 10.0 \text{ M}$
- What must the concentration of water be for a mixture with $[\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5] = 2.0 \text{ M}$, $[\text{CH}_3\text{CO}_2\text{H}] = 0.10 \text{ M}$, $[\text{C}_2\text{H}_5\text{OH}] = 5.0 \text{ M}$ to be at equilibrium?
- Why is water included in the equilibrium expression for this reaction?

39. The equilibrium constant, K , for the reaction



has the value 2.1×10^3 at a particular temperature. When the system is analyzed at equilibrium at this temperature, the concentrations of $\text{H}_2(\text{g})$ and $\text{F}_2(\text{g})$ are both found to be 0.0021 M . What is the concentration of $\text{HF}(\text{g})$ in the equilibrium system under these conditions?

40. The reaction



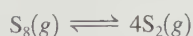
has $K_p = 109$ at 25°C . If the equilibrium partial pressure of Br_2 is 0.0159 atm and the equilibrium partial pressure of NOBr is 0.0768 atm , calculate the partial pressure of NO at equilibrium.

41. A 1.00-L flask was filled with 2.00 mol gaseous SO_2 and 2.00 mol gaseous NO_2 and heated. After equilibrium was reached, it was found that 1.30 mol gaseous NO was present. Assume that the reaction



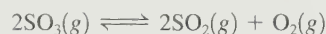
occurs under these conditions. Calculate the value of the equilibrium constant, K , for this reaction.

42. A sample of $\text{S}_8(\text{g})$ is placed in an otherwise empty rigid container at 1325 K at an initial pressure of 1.00 atm , where it decomposes to $\text{S}_2(\text{g})$ by the reaction



At equilibrium, the partial pressure of S_8 is 0.25 atm . Calculate K_p for this reaction at 1325 K .

43. At a particular temperature, 12.0 mol of SO_3 is placed into a 3.0-L rigid container, and the SO_3 dissociates by the reaction



At equilibrium, 3.0 mol of SO_2 is present. Calculate K for this reaction.

44. At a certain temperature, 4.0 mol NH_3 is introduced into a 2.0-L container, and the NH_3 partially dissociates by the reaction



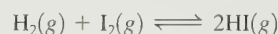
At equilibrium, 2.0 mol NH_3 remains. What is the value of K for this reaction?

45. At a particular temperature, $K = 3.75$ for the reaction



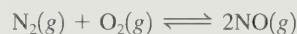
If all four gases had initial concentrations of 0.800 M , calculate the equilibrium concentrations of the gases.

46. At a particular temperature, $K = 1.00 \times 10^2$ for the reaction



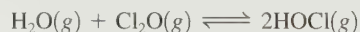
In an experiment, 1.00 mol H_2 , 1.00 mol I_2 , and 1.00 mol HI are introduced into a 1.00-L container. Calculate the concentrations of all species when equilibrium is reached.

47. At 2200°C , $K_p = 0.050$ for the reaction



What is the partial pressure of NO in equilibrium with N_2 and O_2 that were placed in a flask at initial pressures of 0.80 and 0.20 atm , respectively?

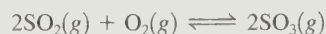
48. At 25°C , $K = 0.090$ for the reaction



Calculate the concentrations of all species at equilibrium for each of the following cases.

- 1.0 g H_2O and 2.0 g Cl_2O are mixed in a 1.0-L flask.
- 1.0 mol pure HOCl is placed in a 2.0-L flask.

49. At 1100 K , $K_p = 0.25$ for the reaction



Calculate the equilibrium partial pressures of SO_2 , O_2 , and SO_3 produced from an initial mixture in which $P_{\text{SO}_2} = P_{\text{O}_2} = 0.50 \text{ atm}$ and $P_{\text{SO}_3} = 0$. (*Hint:* If you don't have a graphing calculator, then use the method of successive approximations to solve, as discussed in Appendix 1.4.)

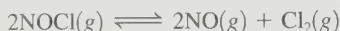
50. At a particular temperature, $K_p = 0.25$ for the reaction



- A flask containing only N_2O_4 at an initial pressure of 4.5 atm is allowed to reach equilibrium. Calculate the equilibrium partial pressures of the gases.

- b. A flask containing only NO_2 at an initial pressure of 9.0 atm is allowed to reach equilibrium. Calculate the equilibrium partial pressures of the gases.
- c. From your answers to parts a and b, does it matter from which direction an equilibrium position is reached?

51. At 35°C , $K = 1.6 \times 10^{-5}$ for the reaction



Calculate the concentrations of all species at equilibrium for each of the following original mixtures.

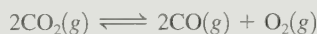
- a. 2.0 mol pure NOCl in a 2.0-L flask
- b. 1.0 mol NOCl and 1.0 mol NO in a 1.0-L flask
- c. 2.0 mol NOCl and 1.0 mol Cl_2 in a 1.0-L flask

52. At a particular temperature, $K = 4.0 \times 10^{-7}$ for the reaction



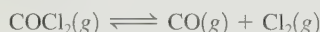
In an experiment, 1.0 mol N_2O_4 is placed in a 10.0-L vessel. Calculate the concentrations of N_2O_4 and NO_2 when this reaction reaches equilibrium.

53. At a particular temperature, $K = 2.0 \times 10^{-6}$ for the reaction



If 2.0 mol CO_2 is initially placed into a 5.0-L vessel, calculate the equilibrium concentrations of all species.

54. Lexan is a plastic used to make compact discs, eyeglass lenses, and bullet-proof glass. One of the compounds used to make Lexan is phosgene (COCl_2), an extremely poisonous gas. Phosgene decomposes by the reaction



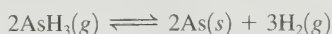
for which $K_p = 6.8 \times 10^{-9}$ at 100°C . If pure phosgene at an initial pressure of 1.0 atm decomposes, calculate the equilibrium pressures of all species.

55. At 25°C , $K_p = 2.9 \times 10^{-3}$ for the reaction



In an experiment carried out at 25°C , a certain amount of $\text{NH}_4\text{OCONH}_2$ is placed in an evacuated rigid container and allowed to come to equilibrium. Calculate the total pressure in the container at equilibrium.

56. The gas arsine, AsH_3 , decomposes as follows:

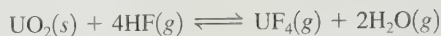


In an experiment at a certain temperature, pure $\text{AsH}_3(g)$ was placed in an empty, rigid, sealed flask at a pressure of 392.0 torr. After 48 hours the pressure in the flask was observed to be constant at 488.0 torr.

- a. Calculate the equilibrium pressure of $\text{H}_2(g)$
- b. Calculate K_p for this reaction.

Le Châtelier's Principle

57. Suppose the reaction system



has already reached equilibrium. Predict the effect that each of the following changes has on the equilibrium position. Tell whether the equilibrium will shift to the right, will shift to the left, or will not be affected.

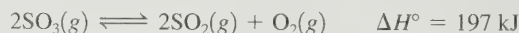
- a. Additional $\text{UO}_2(s)$ is added to the system.
- b. The reaction is performed in a glass reaction vessel; $\text{HF}(g)$ attacks and reacts with glass.
- c. Water vapor is removed.
58. Predict the shift in the equilibrium position that will occur for each of the following reactions when the volume of the reaction container is increased.
- a. $\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)$
- b. $\text{PCl}_5(g) \rightleftharpoons \text{PCl}_3(g) + \text{Cl}_2(g)$
- c. $\text{H}_2(g) + \text{F}_2(g) \rightleftharpoons 2\text{HF}(g)$
- d. $\text{COCl}_2(g) \rightleftharpoons \text{CO}(g) + \text{Cl}_2(g)$
- e. $\text{CaCO}_3(s) \rightleftharpoons \text{CaO}(s) + \text{CO}_2(g)$

59. An important reaction in the commercial production of hydrogen is



How will this system at equilibrium shift in each of the five following cases?

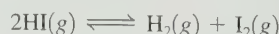
- a. Gaseous carbon dioxide is removed.
- b. Water vapor is added.
- c. The pressure is increased by adding helium gas.
- d. The temperature is increased (the reaction is exothermic).
- e. The pressure is increased by decreasing the volume of the reaction container.
60. What will happen to the number of moles of SO_3 in equilibrium with SO_2 and O_2 in the reaction



in each of the following cases?

- a. Oxygen gas is added.
- b. The pressure is increased by decreasing the volume of the reaction container.
- c. The pressure is increased by adding argon gas.
- d. The temperature is decreased.
- e. Gaseous sulfur dioxide is removed.

61. In which direction will the position of the equilibrium

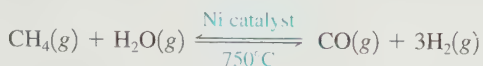


be shifted for each of the following changes?

- a. $\text{H}_2(g)$ is added.
- b. $\text{I}_2(g)$ is removed.
- c. $\text{HI}(g)$ is removed.

- d. Some Ar(g) is added.
- e. The volume of the container is doubled.
- f. The temperature is decreased (the reaction is exothermic).

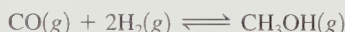
62. Hydrogen for use in ammonia production is produced by the reaction



What will happen to a reaction mixture at equilibrium if

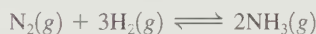
- a. $\text{H}_2\text{O}(\text{g})$ is removed?
- b. the temperature is increased (the reaction is endothermic)?
- c. an inert gas is added?
- d. $\text{CO}(\text{g})$ is removed?
- e. the volume of the container is tripled?

63. The reaction to prepare methanol from hydrogen and carbon monoxide



is exothermic. If you wanted to use this reaction for producing methanol commercially, would high or low temperatures favor a maximum yield?

64. Ammonia is produced by the Haber process, in which nitrogen and hydrogen are reacted directly using an iron mesh impregnated with oxides as a catalyst. For the reaction



equilibrium constants (K_p values) as a function of temperature are

$$300^\circ\text{C.} \quad 4.34 \times 10^{-3}$$

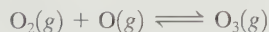
$$500^\circ\text{C.} \quad 1.45 \times 10^{-5}$$

$$600^\circ\text{C.} \quad 2.25 \times 10^{-6}$$

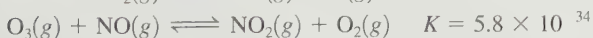
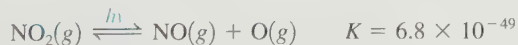
Is the reaction exothermic or endothermic?

Additional Exercises

65. Calculate a value for the equilibrium constant for the reaction

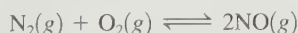


given



Hint: When reactions are added together, the equilibrium expressions are multiplied.

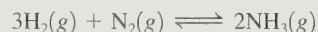
66. At 25°C , $K_p \approx 1 \times 10^{-31}$ for the reaction



- a. Calculate the concentration of NO, in molecules/cm³, that can exist in equilibrium in air at 25°C . In air, $P_{\text{N}_2} = 0.8$ atm and $P_{\text{O}_2} = 0.2$ atm.

- b. Typical concentrations of NO in relatively pristine environments range from 10^8 to 10^{10} molecules/cm³. Why is there a discrepancy between these values and your answer to part a?

67. An initial mixture of nitrogen gas and hydrogen gas is reacted in a rigid container at a certain temperature by the reaction



At equilibrium, the concentrations are $[\text{H}_2] = 5.0 \text{ M}$, $[\text{N}_2] = 8.0 \text{ M}$, and $[\text{NH}_3] = 4.0 \text{ M}$. What were the concentrations of nitrogen gas and hydrogen gas that were reacted initially?

68. At a certain temperature, $K = 9.1 \times 10^{-4}$ for the reaction



Calculate the concentrations of Fe^{3+} , SCN^{-} , and FeSCN^{2+} in a solution that is initially 2.0 M FeSCN^{2+} .

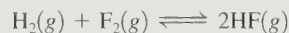
69. For the reaction



at $600. \text{ K}$, the equilibrium constant, K_p , is 11.5 . Suppose that 2.450 g of PCl_5 is placed in an evacuated 500-mL bulb, which is then heated to $600. \text{ K}$.

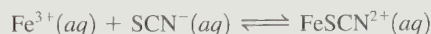
- a. What would be the pressure of PCl_5 if it did not dissociate?
 - b. What is the partial pressure of PCl_5 at equilibrium?
 - c. What is the total pressure in the bulb at equilibrium?
 - d. What is the degree of dissociation of PCl_5 at equilibrium?
70. At 25°C , gaseous SO_2Cl_2 decomposes to $\text{SO}_2(\text{g})$ and $\text{Cl}_2(\text{g})$ to the extent that 12.5% of the original SO_2Cl_2 (by moles) has decomposed to reach equilibrium. The total pressure (at equilibrium) is 0.900 atm . Calculate the value of K_p for this system.

71. For the following reaction at a certain temperature



it is found that the equilibrium concentrations in a 5.00-L rigid container are $[\text{H}_2] = 0.0500 \text{ M}$, $[\text{F}_2] = 0.0100 \text{ M}$, and $[\text{HF}] = 0.400 \text{ M}$. If 0.200 mol of F_2 is added to this equilibrium mixture, calculate the concentrations of all gases once equilibrium is reestablished.

72. Consider the reaction



How will the equilibrium position shift if

- a. water is added, doubling the volume?
 - b. $\text{AgNO}_3(\text{aq})$ is added? (AgSCN is insoluble.)
 - c. $\text{NaOH}(\text{aq})$ is added? [$\text{Fe}(\text{OH})_3$ is insoluble.]
 - d. $\text{Fe}(\text{NO}_3)_3(\text{aq})$ is added?
73. Chromium(VI) forms two different oxyanions, the orange dichromate ion, $\text{Cr}_2\text{O}_7^{2-}$, and the yellow chromate ion, CrO_4^{2-} . (See the photos on the following page.) The equilibrium reaction between the two ions is



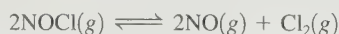
Explain why orange dichromate solutions turn yellow when sodium hydroxide is added.



74. The synthesis of ammonia gas from nitrogen gas and hydrogen gas represents a classic case in which a knowledge of kinetics and equilibrium was used to make a desired chemical reaction economically feasible. Explain how each of the following conditions helps to maximize the yield of ammonia.
- running the reaction at an elevated temperature
 - removing the ammonia from the reaction mixture as it forms
 - using a catalyst
 - running the reaction at high pressure

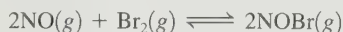
Challenge Problems

75. At 35°C , $K = 1.6 \times 10^{-5}$ for the reaction

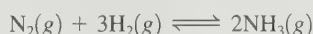


If 2.0 mol NO and 1.0 mol Cl_2 are placed into a 1.0-L flask, calculate the equilibrium concentrations of all species.

76. Nitric oxide and bromine at initial partial pressures of 98.4 and 41.3 torr, respectively, were allowed to react at 300. K. At equilibrium the total pressure was 110.5 torr. The reaction is



- Calculate the value of K_p .
 - What would be the partial pressures of all species if NO and Br_2 , both at an initial partial pressure of 0.30 atm, were allowed to come to equilibrium at this temperature?
77. At 25°C , $K_p = 5.3 \times 10^5$ for the reaction



When a certain partial pressure of $\text{NH}_3(g)$ is put into an otherwise empty rigid vessel at 25°C , equilibrium is reached when 50.0% of the original ammonia has decomposed. What was the original partial pressure of ammonia before any decomposition occurred?

78. Consider the reaction



where $K_p = 1.00 \times 10^{-1}$ at 1325 K. In an experiment where $\text{P}_4(g)$ is placed into a container at 1325 K, the equilibrium mixture of $\text{P}_4(g)$ and $\text{P}_2(g)$ has a total pressure of 1.00 atm. Calculate the equilibrium pressures of $\text{P}_4(g)$ and $\text{P}_2(g)$. Calculate the fraction (by moles) of $\text{P}_4(g)$ that has dissociated to reach equilibrium.

79. The partial pressures of an equilibrium mixture of $\text{N}_2\text{O}_4(g)$ and $\text{NO}_2(g)$ are $P_{\text{N}_2\text{O}_4} = 0.34$ atm and $P_{\text{NO}_2} = 1.20$ atm at a certain temperature. The volume of the container is doubled. Find the partial pressures of the two gases when a new equilibrium is established.
80. At 125°C , $K_p = 0.25$ for the reaction



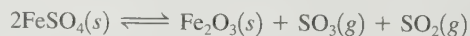
A 1.00-L flask containing 10.0 g NaHCO_3 is evacuated and heated to 125°C .

- Calculate the partial pressures of CO_2 and H_2O after equilibrium is established.
 - Calculate the masses of NaHCO_3 and Na_2CO_3 present at equilibrium.
 - Calculate the minimum container volume necessary for all of the NaHCO_3 to decompose.
81. An 8.00-g sample of SO_3 was placed in an evacuated container, where it decomposed at 600°C according to the following reaction:



At equilibrium the total pressure and the density of the gaseous mixture were 1.80 atm and 1.60 g/L, respectively. Calculate K_p for this reaction.

82. A sample of iron(II) sulfate was heated in an evacuated container to 920 K, where the following reactions occurred:



After equilibrium was reached, the total pressure was 0.836 atm and the partial pressure of oxygen was 0.0275 atm. Calculate K_p for each of these reactions.

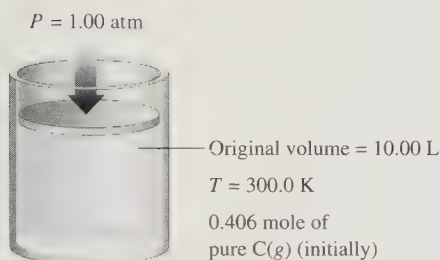
Marathon Problem*

This problem is designed to incorporate several concepts and techniques into one situation. Marathon Problems can be used in class by groups of students to help facilitate problem-solving skills.

83. Consider the reaction



for which $K = 1.30 \times 10^2$. Assume that 0.406 mol $C(g)$ is placed in the cylinder represented below. The temperature is 300.0 K, and the barometric pressure on the piston (which is assumed to be massless and frictionless) is constant at 1.00 atm. The original volume (before the 0.406 mol $C(g)$ begins to decompose) is 10.00 L. What is the volume in the cylinder at equilibrium?



Media Activities

1. a. Open the Equilibrium Decomposition of N_2O_4 Visualization on the student CD. Equilibrium is a dynamic process. What does this mean? For a reaction at equilibrium, what is true about the rate of the forward and reverse reactions and what is true about the concentrations of reactants and products?
- b. The visualization examines the N_2O_4 equilibrium as well as the effect of temperature on this equilibrium. For the reaction $N_2O_4(g) \rightleftharpoons 2 NO_2(g)$, what is the equilibrium constant expression (K) in terms of molarity concentration units? What is the equilibrium constant expression (K_p) in terms of partial pressures? As long as temperature remains constant, the values of K and K_p remain constant no matter what initial concentrations of reactants or products are used. However, when temperature changes, the values of K and

K_p change. From the N_2O_4 animation, did the value of K (or K_p) increase or decrease as temperature increased? (Hint: Compare the amount of NO_2 and N_2O_4 present at equilibrium before and after the heating.)

2. a. Open the Equilibrium Understanding Concepts activity on the student CD and read the introduction to review Le Châtelier's principle. When a reactant or product is added, the reaction shifts to reestablish equilibrium. Does the value of K change when a reactant or product is added? For a gaseous reaction, does the value of K change when the container volume is changed? Consider the reaction $N_2O_4(g) \rightleftharpoons 2 NO_2(g)$. If the total pressure of the system at equilibrium is doubled by halving the volume, which way will the reaction shift to reestablish equilibrium? If the total pressure of the system at equilibrium is doubled by adding an inert gas like He, what effect does this have on the equilibrium?
- b. Next, go through the example, which examines the $Fe^{3+} + NCS^- \rightleftharpoons FeNCS^{2+}$ equilibrium. The exercises study the effect of adding several reagents to this equilibrium. Your job is to use Le Châtelier's principle to predict which way the reaction shifts with each reagent added. It's important to know the color of solution when the hydrated Fe^{3+} dominates and the color of solution when $FeNCS^{2+}$ dominates. What color is each of these species?
- c. Go through all eight exercises and predict which way the reaction shifts to reestablish equilibrium. Also predict the color change that should occur. Play the reaction to verify your answer and choose Why to see a detailed explanation. The effects that some of the reagent additions will have are not obvious. Here are some hints to help you deduce what should happen:

Addition of tin(II) chloride: Sn^{2+} reacts with Fe^{3+} to produce Sn^{4+} and Fe^{2+} .

Addition of silver nitrate: Ag^+ reacts with NCS^- to produce solid $AgNCS$.

Addition of sodium hydrogen phosphate: HPO_4^{2-} reacts with Fe^{3+} to produce $FeHPO_4^+$.

Addition of ammonia: The weak base NH_3 produces OH^- which reacts with Fe^{3+} to produce solid $Fe(OH)_3$.

Addition of heat: The reaction is exothermic.

- d. The value of K changes for a reaction when temperature changes. For an exothermic reaction, does K increase or decrease when temperature increases? For an endothermic reaction, does K increase or decrease when temperature increases? For more practice with Le Châtelier's principle, do Exercises 13.59, 13.61, 13.63, and 13.64 in the text.
3. Test your understanding of Chapter 13 material by taking the ACE quizzes on the student web site.

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For additional web activities and other resources, visit the Zumdahl, *Chemistry*, Sixth Edition textbook site at <http://chemistry.college.hmco.com/students>.



Acids and Bases

In this chapter we reencounter two very important classes of compounds, acids and bases. We will explore their interactions and apply the fundamentals of chemical equilibria discussed in Chapter 13 to systems involving proton-transfer reactions.

Acid–base chemistry is important in a wide variety of everyday applications. There are complex systems in our bodies that carefully control the acidity of our blood, since even small deviations may lead to serious illness and death. The same sensitivity exists in other life forms. If you have ever had tropical fish or goldfish, you know how important it is to monitor and control the acidity of the water in the aquarium.

Acids and bases are also important in industry. For example, the vast quantity of sulfuric acid manufactured in the United States each year is needed to produce fertilizers, polymers, steel, and many other materials.

The influence of acids on living things has assumed special importance in the United States, Canada, and Europe in recent years as a result of the phenomenon of acid rain (see the Chemical Impact in Chapter 5). This problem is complex and has diplomatic and economic overtones that make it all the more difficult to solve.

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- 14.1 The Nature of Acids and Bases**
- 14.2 Acid Strength**
 - Water as an Acid and a Base
- 14.3 The pH Scale**
- 14.4 Calculating the pH of Strong Acid Solutions**
- 14.5 Calculating the pH of Weak Acid Solutions**
 - The pH of a Mixture of Weak Acids
 - Percent Dissociation
- 14.6 Bases**
- 14.7 Polyprotic Acids**
 - Phosphoric Acid
 - Sulfuric Acid
- 14.8 Acid–Base Properties of Salts**
 - Salts That Produce Neutral Solutions
 - Salts That Produce Basic Solutions
 - Base Strength in Aqueous Solution
 - Salts That Produce Acidic Solutions
- 14.9 The Effect of Structure on Acid–Base Properties**
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- 14.11 The Lewis Acid–Base Model**
- 14.12 Strategy for Solving Acid–Base Problems: A Summary**

14.1 The Nature of Acids and Bases

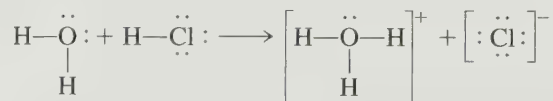
Don't taste chemicals!

Acids and bases were first discussed in Section 4.2.

Acids were first recognized as a class of substances that taste sour. Vinegar tastes sour because it is a dilute solution of acetic acid; citric acid is responsible for the sour taste of a lemon. Bases, sometimes called *alkalis*, are characterized by their bitter taste and slippery feel. Commercial preparations for unclogging drains are highly basic.

The first person to recognize the essential nature of acids and bases was Svante Arrhenius. Based on his experiments with electrolytes, Arrhenius postulated that *acids produce hydrogen ions in aqueous solution; while bases produce hydroxide ions*. At the time, the **Arrhenius concept** of acids and bases was a major step forward in quantifying acid–base chemistry, but this concept is limited because it applies only to aqueous solutions and allows for only one kind of base—the hydroxide ion. A more general definition of acids and bases was suggested by the Danish chemist Johannes Brønsted (1879–1947) and the English chemist Thomas Lowry (1874–1936). In terms of the **Brønsted–Lowry model**, *an acid is a proton (H^+) donor, and a base is a proton acceptor*. For example, when gaseous HCl dissolves in water, each HCl molecule donates a proton to a water molecule and so qualifies as a Brønsted–Lowry acid. The molecule that accepts the proton, in this case water, is a Brønsted–Lowry base.

To understand how water can act as a base, we need to remember that the oxygen of the water molecule has two unshared electron pairs, either of which can form a covalent bond with an H^+ ion. When gaseous HCl dissolves, the following reaction occurs:

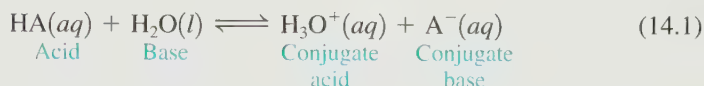


Common household substances that contain acids and bases. Vinegar is a dilute solution of acetic acid. Drain cleaners contain strong bases such as sodium hydroxide.

FIGURE 14.1The reaction of HCl and H₂O.

Note that the proton is transferred from the HCl molecule to the water molecule to form H₃O⁺, which is called the **hydronium ion**. This reaction is represented in Fig. 14.1 using molecular models.

The general reaction that occurs when an acid is dissolved in water can best be represented as



Recall that (aq) means the substance is hydrated.

This representation emphasizes the significant role of the polar water molecule in pulling the proton from the acid. Note that the **conjugate base** is everything that remains of the acid molecule after a proton is lost. The **conjugate acid** is formed when the proton is transferred to the base. A **conjugate acid–base pair** consists of two substances related to each other by the donating and accepting of a single proton. In Equation (14.1) there are two conjugate acid–base pairs: HA and A[−] and H₂O and H₃O⁺. This reaction is represented by molecular models in Fig. 14.2.

It is important to note that Equation (14.1) really represents *a competition for the proton between the two bases H₂O and A[−]*. If H₂O is a much stronger base than A[−], that is, if H₂O has a much greater affinity for H⁺ than does A[−], the equilibrium position will be far to the right; most of the acid dissolved will be in the ionized form. Conversely, if A[−] is a much stronger base than H₂O, the equilibrium position will lie far to the left. In this case most of the acid dissolved will be present at equilibrium as HA.

The equilibrium expression for the reaction given in Equation (14.1) is

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \quad (14.2)$$

In this chapter we will always represent an acid as simply dissociating. This does not mean we are using the Arrhenius model for acids. Since water does not affect the equilibrium position, it is simply easier to leave it out of the acid dissociation reaction.

where K_a is called the **acid dissociation constant**. Both H₃O⁺(aq) and H⁺(aq) are commonly used to represent the hydrated proton. In this book we will often use simply H⁺, but you should remember that it is hydrated in aqueous solutions.

In Chapter 13 we saw that the concentration of a pure solid or a pure liquid is always omitted from the equilibrium expression. In a dilute solution we can assume that the concentration of liquid water remains essentially constant when an acid is dissolved. Thus the term [H₂O] is not included in Equation (14.2), and the equilibrium expression for K_a has the same form as that for the simple dissociation into ions:



You should not forget, however, that water plays an important role in causing the acid to ionize.

FIGURE 14.2

The reaction of an acid HA with water to form H₃O⁺ and a conjugate base A[−].



Note that K_a is the equilibrium constant for the reaction in which a proton is removed from HA to form the conjugate base A^- . We use K_a to represent *only* this type of reaction. Knowing this, you can write the K_a expression for any acid, even one that is totally unfamiliar to you. As you do Sample Exercise 14.1, focus on the definition of the reaction corresponding to K_a .

SAMPLE EXERCISE 14.1

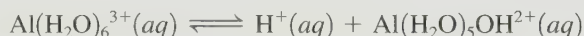
Acid Dissociation (Ionization) Reactions

Write the simple dissociation (ionization) reaction (omitting water) for each of the following acids.

- Hydrochloric acid (HCl)
- Acetic acid ($\text{HC}_2\text{H}_3\text{O}_2$)
- The ammonium ion (NH_4^+)
- The anilinium ion ($\text{C}_6\text{H}_5\text{NH}_3^+$)
- The hydrated aluminum(III) ion $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$

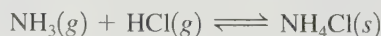
SOLUTION

- $\text{HCl}(aq) \rightleftharpoons \text{H}^+(aq) + \text{Cl}^-(aq)$
- $\text{HC}_2\text{H}_3\text{O}_2(aq) \rightleftharpoons \text{H}^+(aq) + \text{C}_2\text{H}_3\text{O}_2^-(aq)$
- $\text{NH}_4^+(aq) \rightleftharpoons \text{H}^+(aq) + \text{NH}_3(aq)$
- $\text{C}_6\text{H}_5\text{NH}_3^+(aq) \rightleftharpoons \text{H}^+(aq) + \text{C}_6\text{H}_5\text{NH}_2(aq)$
- Although this formula looks complicated, writing the reaction is simple if you concentrate on the meaning of K_a . Removing a proton, which can come only from one of the water molecules, leaves one OH^- and five H_2O molecules attached to the Al^{3+} ion. So the reaction is

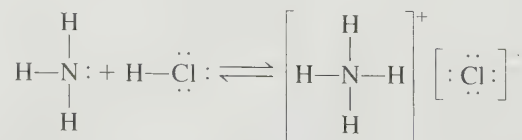


See Exercises 14.29 and 14.30.

The Brønsted–Lowry model is not limited to aqueous solutions; it can be extended to reactions in the gas phase. For example, we discussed the reaction between gaseous hydrogen chloride and ammonia when we studied diffusion (Section 5.7):



In this reaction, a proton is donated by the hydrogen chloride to the ammonia, as shown by these Lewis structures:



Note that this is not considered an acid–base reaction according to the Arrhenius concept. Figure 14.3 shows a molecular representation of this reaction.



FIGURE 14.3

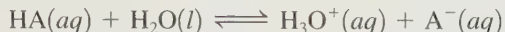
The reaction of NH_3 with HCl to form NH_4^+ and Cl^- .

14.2 Acid Strength



Understanding Concepts: Weak and Strong Acids

The strength of an acid is defined by the equilibrium position of its dissociation (ionization) reaction:



A **strong acid** is one for which *this equilibrium lies far to the right*. This means that almost all the original HA is dissociated (ionized) at equilibrium [see Fig. 14.4(a)]. There is an important connection between the strength of an acid and that of its conjugate base. A *strong acid yields a weak conjugate base*—one that has a low affinity for a proton. A strong acid also can be described as an acid whose conjugate base is a much weaker base than water (see Fig. 14.5). In this case the water molecules win the competition for the H^+ ions.

Conversely, a **weak acid** is one for which *the equilibrium lies far to the left*. Most of the acid originally placed in the solution is still present as HA at equilibrium. That is, a weak acid dissociates only to a very small extent in aqueous solution [see Fig. 14.4(b)]. In contrast to a strong acid, a weak acid has a conjugate base that is a much stronger base than water. In this case a water molecule is not very successful in pulling an H^+ ion from the conjugate base. *The weaker the acid, the stronger its conjugate base*.

The various ways of describing the strength of an acid are summarized in Table 14.1. Strong and weak acids are represented pictorially in Fig. 14.6.

The common strong acids are sulfuric acid [$\text{H}_2\text{SO}_4(aq)$], hydrochloric acid [$\text{HCl}(aq)$], nitric acid [$\text{HNO}_3(aq)$], and perchloric acid [$\text{HClO}_4(aq)$]. Sulfuric acid is actually a **diprotic acid**, an acid having two acidic protons. The acid H_2SO_4 is a strong acid, virtually 100% dissociated (ionized) in water:

A strong acid has a weak conjugate base.

Perchloric acid can explode if handled improperly.

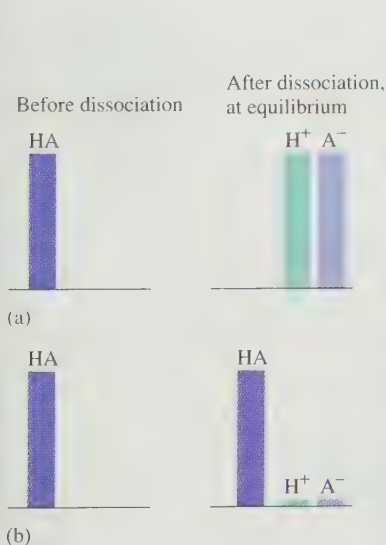


FIGURE 14.4

Graphic representation of the behavior of acids of different strengths in aqueous solution. (a) A strong acid. (b) A weak acid.

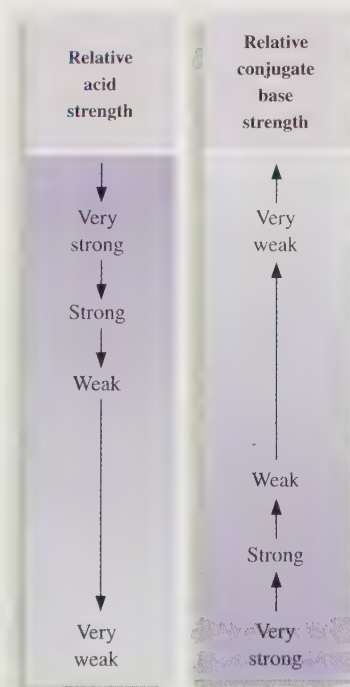
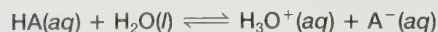


FIGURE 14.5

The relationship of acid strength and conjugate base strength for the reaction



Acid

Conjugate base

TABLE 14.1 Various Ways to Describe Acid Strength

Property	Strong Acid	Weak Acid
K_a value	K_a is large	K_a is small
Position of the dissociation (ionization) equilibrium	Far to the right	Far to the left
Equilibrium concentration of H^+ compared with original concentration of HA	$[H^+] \approx [HA]_0$	$[H^+] \ll [HA]_0$
Strength of conjugate base compared with that of water	A^- much weaker base than H_2O	A^- much stronger base than H_2O

$\ll$ means much less than.
 $\gg$ means much greater than.

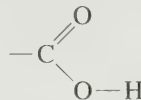


The HSO_4^- ion, however, is a weak acid:

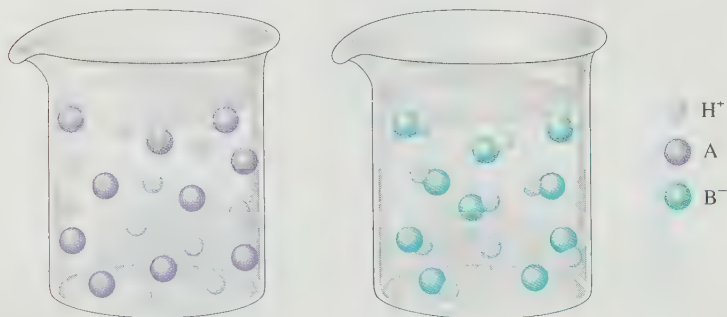
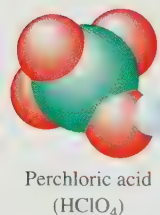
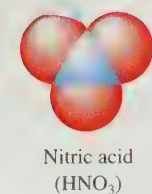
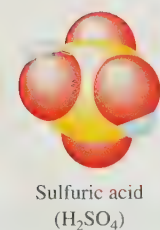


Appendix 5.1 contains a table of K_a values.

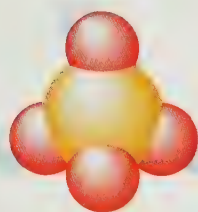
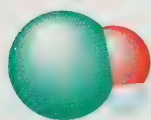
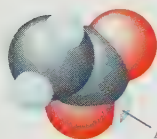
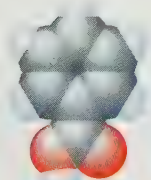
Most acids are **oxyacids**, in which the acidic proton is attached to an oxygen atom. The strong acids mentioned above, except hydrochloric acid, are typical examples. Many common weak acids, such as phosphoric acid (H_3PO_4), nitrous acid (HNO_2), and hypochlorous acid ($HOCl$), are also oxyacids. **Organic acids**, those with a carbon atom backbone, commonly contain the **carboxyl group**:



Acids of this type are usually weak. Examples are acetic acid (CH_3COOH), often written $HC_2H_3O_2$, and benzoic acid (C_6H_5COOH). Note that the remainder of the hydrogens in these molecules are not acidic—they do not form H^+ in water.

**FIGURE 14.6**

(a) A strong acid HA is completely ionized in water. (b) A weak acid HB exists mostly as undissociated HB molecules in water. Note that the water molecules are not shown in this figure.

Phosphoric acid
(H_3PO_4)Nitrous acid
(HNO_2)Hypochlorous acid
(HOCl)Acetic acid
($\text{CH}_3\text{CO}_2\text{H}$)Benzoic acid
($\text{C}_6\text{H}_5\text{CO}_2\text{H}$)**TABLE 14.2** Values of K_a for Some Common Monoprotic Acids

Formula	Name	Value of K_a^*	Increasing acid strength ↑
HSO_4^-	Hydrogen sulfate ion	1.2×10^{-2}	
HClO_2	Chlorous acid	1.2×10^{-2}	
$\text{HC}_2\text{H}_2\text{ClO}_2$	Monochloroacetic acid	1.35×10^{-3}	
HF	Hydrofluoric acid	7.2×10^{-4}	
HNO_2	Nitrous acid	4.0×10^{-4}	
$\text{HC}_2\text{H}_3\text{O}_2$	Acetic acid	1.8×10^{-5}	
$[\text{Al}(\text{H}_2\text{O})_6]^{3+}$	Hydrated aluminum(III) ion	1.4×10^{-5}	
HOCl	Hypochlorous acid	3.5×10^{-8}	
HCN	Hydrocyanic acid	6.2×10^{-10}	
NH_4^+	Ammonium ion	5.6×10^{-10}	
HOC_6H_5	Phenol	1.6×10^{-10}	

*The units of K_a are customarily omitted.

There are some important acids in which the acidic proton is attached to an atom other than oxygen. The most significant of these are the hydrohalic acids HX , where X represents a halogen atom.

Table 14.2 contains a list of common **monoprotic acids** (those having *one* acidic proton) and their K_a values. Note that the strong acids are not listed. When a strong acid molecule such as HCl , for example, is placed in water, the position of the dissociation equilibrium



lies so far to the right that $[\text{HCl}]$ cannot be measured accurately. This prevents an accurate calculation of K_a :

$$K_a = \frac{[\text{H}^+][\text{Cl}^-]}{[\text{HCl}]}$$

↖ Very small and highly uncertain

SAMPLE EXERCISE 14.2

Relative Base Strength

Using Table 14.2, arrange the following species according to their strengths as bases: H_2O , F^- , Cl^- , NO_2^- , and CN^- .

SOLUTION

Remember that water is a stronger base than the conjugate base of a strong acid but a weaker base than the conjugate base of a weak acid. This leads to the following order:



Visualization: Neutralization of a Strong Acid by a Strong Base

We can order the remaining conjugate bases by recognizing that the strength of an acid is *inversely related* to the strength of its conjugate base. Since from Table 14.2 we have

$$K_a \text{ for HF} > K_a \text{ for HNO}_2 > K_a \text{ for HCN}$$

the base strengths increase as follows:

$$\text{F}^- < \text{NO}_2^- < \text{CN}^-$$

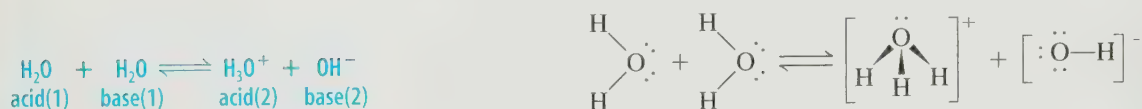
The combined order of increasing base strength is

$$\text{Cl}^- < \text{H}_2\text{O} < \text{F}^- < \text{NO}_2^- < \text{CN}^-$$

See Exercises 14.35 through 14.38.

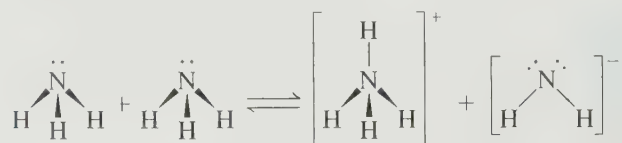
Water as an Acid and a Base

A substance is said to be **amphoteric** if it can behave either as an acid or as a base. Water is the most common **amphoteric substance**. We can see this clearly in the **autoionization** of water, which involves the transfer of a proton from one water molecule to another to produce a hydroxide ion and a hydronium ion:



In this reaction, also illustrated in Fig. 14.7, one water molecule acts as an acid by furnishing a proton, and the other acts as a base by accepting the proton.

Autoionization can occur in other liquids besides water. For example, in liquid ammonia the autoionization reaction is



The autoionization reaction for water



leads to the equilibrium expression

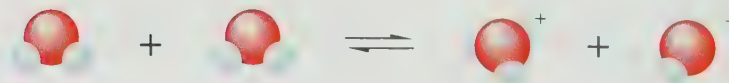
$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = [\text{H}^+][\text{OH}^-]$$

where K_w , called the **ion-product constant** (or the **dissociation constant** for water), always refers to the autoionization of water.

Experiment shows that at 25°C in pure water,

$$[\text{H}^+] = [\text{OH}^-] = 1.0 \times 10^{-7} M$$

FIGURE 14.7
Two water molecules react to form H_3O^+ and OH^- .



which means that at 25°C

$$K_w = [\text{H}^+][\text{OH}^-] \\ = 1.0 \times 10^{-14}$$

$$K_w = [\text{H}^+][\text{OH}^-] = (1.0 \times 10^{-7})(1.0 \times 10^{-7}) \\ = 1.0 \times 10^{-14}$$

It is important to recognize the meaning of K_w . In any aqueous solution at 25°C, *no matter what it contains*, the product of $[\text{H}^+]$ and $[\text{OH}^-]$ must always equal 1.0×10^{-14} . There are three possible situations:

1. A neutral solution, where $[\text{H}^+] = [\text{OH}^-]$.
2. An acidic solution, where $[\text{H}^+] > [\text{OH}^-]$.
3. A basic solution, where $[\text{OH}^-] > [\text{H}^+]$.

In each case, however, at 25°C,

$$K_w = [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14}$$

SAMPLE EXERCISE 14.3

Calculating $[\text{H}^+]$ and $[\text{OH}^-]$

Calculate $[\text{H}^+]$ or $[\text{OH}^-]$ as required for each of the following solutions at 25°C, and state whether the solution is neutral, acidic, or basic.

- $1.0 \times 10^{-5} \text{ M OH}^-$
- $1.0 \times 10^{-7} \text{ M OH}^-$
- 10.0 M H^+

SOLUTION

- a. $K_w = [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14}$. Since $[\text{OH}^-]$ is $1.0 \times 10^{-5} \text{ M}$, solving for $[\text{H}^+]$ gives

$$[\text{H}^+] = \frac{1.0 \times 10^{-14}}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-5}} = 1.0 \times 10^{-9} \text{ M}$$

Since $[\text{OH}^-] > [\text{H}^+]$, the solution is basic.

- b. As in part a, solving for $[\text{H}^+]$ gives

$$[\text{H}^+] = \frac{1.0 \times 10^{-14}}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-7}} = 1.0 \times 10^{-7} \text{ M}$$

Since $[\text{H}^+] = [\text{OH}^-]$, the solution is neutral.

- c. Solving for $[\text{OH}^-]$ gives

$$[\text{OH}^-] = \frac{1.0 \times 10^{-14}}{[\text{H}^+]} = \frac{1.0 \times 10^{-14}}{10.0} = 1.0 \times 10^{-15} \text{ M}$$

Since $[\text{H}^+] > [\text{OH}^-]$, the solution is acidic.

See Exercises 14.39 and 14.40.



Visualization: Self-Ionization of Water to Form H^+ and OH^- in Equilibrium

Since K_w is an equilibrium constant, it varies with temperature. The effect of temperature is considered in Sample Exercise 14.4.

SAMPLE EXERCISE 14.4

Autoionization of Water

At 60°C, the value of K_w is 1×10^{-13} .

- a. Using Le Châtelier's principle, predict whether the reaction



is exothermic or endothermic.

- b. Calculate $[\text{H}^+]$ and $[\text{OH}^-]$ in a neutral solution at 60°C.

SOLUTION

- a. K_w increases from 1×10^{-14} at 25°C to 1×10^{-13} at 60°C. Le Châtelier's principle states that if a system at equilibrium is heated, it will adjust to consume energy. Since the value of K_w increases with temperature, we must think of energy as a reactant, and so the process must be endothermic.

- b. At 60°C,

$$[\text{H}^+][\text{OH}^-] = 1 \times 10^{-13}$$

For a neutral solution,

$$[\text{H}^+] = [\text{OH}^-] = \sqrt{1 \times 10^{-13}} = 3 \times 10^{-7} M$$

See Exercise 14.41.

14.3 The pH Scale

The pH scale is a compact way to represent solution acidity.

Appendix 1.2 has a review of logs.

Because $[\text{H}^+]$ in an aqueous solution is typically quite small, the **pH scale** provides a convenient way to represent solution acidity. The pH is a log scale based on 10, where

$$\text{pH} = -\log[\text{H}^+]$$

Thus for a solution where

$$[\text{H}^+] = 1.0 \times 10^{-7} M$$

$$\text{pH} = -(-7.00) = 7.00$$

At this point we need to discuss significant figures for logarithms. The rule is that *the number of decimal places in the log is equal to the number of significant figures in the original number*. Thus

$$[\text{H}^+] = 1.0 \times 10^{-9} M \quad \leftarrow 2 \text{ significant figures}$$

$$\text{pH} = 9.00 \quad \leftarrow 2 \text{ decimal places}$$

Similar log scales are used for representing other quantities; for example,

$$\text{pOH} = -\log[\text{OH}^-]$$

$$\text{p}K = -\log K$$

Since pH is a log scale based on 10, *the pH changes by 1 for every power of 10 change in $[\text{H}^+]$* . For example, a solution of pH 3 has an H^+ concentration 10 times that of a solution of pH 4 and 100 times that of a solution of pH 5. Also

note that because pH is defined as $-\log[H^+]$, the pH decreases as $[H^+]$ increases. The pH scale and the pH values for several common substances are shown in Fig. 14.8.

The pH of a solution is usually measured using a pH meter, an electronic device with a probe that can be inserted into a solution of unknown pH. The probe contains an acidic aqueous solution enclosed by a special glass membrane that allows migration of H^+ ions. If the unknown solution has a different pH from the solution in the probe, an electric potential results, which is registered on the meter (see Fig. 14.9).

SAMPLE EXERCISE 14.5

The pH meter is discussed more fully in Section 17.4.

Calculating pH and pOH

Calculate pH and pOH for each of the following solutions at 25°C.

- $1.0 \times 10^{-3} M OH^-$
- $1.0 M H^+$

SOLUTION

$$\text{a.} \quad [H^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-3}} = 1.0 \times 10^{-11} M$$

$$pH = -\log[H^+] = -\log(1.0 \times 10^{-11}) = 11.00$$

$$pOH = -\log[OH^-] = -\log(1.0 \times 10^{-3}) = 3.00$$

$$\text{b.} \quad [OH^-] = \frac{K_w}{[H^+]} = \frac{1.0 \times 10^{-14}}{1.0} = 1.0 \times 10^{-14} M$$

$$pH = -\log[H^+] = -\log(1.0) = 0.00$$

$$pOH = -\log[OH^-] = -\log(1.0 \times 10^{-14}) = 14.00$$

See Exercise 14.43.

It is useful to consider the log form of the expression

$$K_w = [H^+][OH^-]$$

That is,

$$\log K_w = \log[H^+] + \log[OH^-]$$

	$[H^+]$	pH	
	10^{-14}	14	← 1 M NaOH
	10^{-13}	13	
Basic	10^{-12}	12	← Ammonia (Household cleaner)
	10^{-11}	11	
	10^{-10}	10	
	10^{-9}	9	
	10^{-8}	8	
Neutral	10^{-7}	7	← Blood
			← Pure water
			← Milk
	10^{-6}	6	
	10^{-5}	5	
	10^{-4}	4	
	10^{-3}	3	← Vinegar
			← Lemon juice
Acidic	10^{-2}	2	← Stomach acid
	10^{-1}	1	
	1	0	← 1 M HCl

FIGURE 14.8

The pH scale and pH values of some common substances.



FIGURE 14.9

pH meters are used to measure acidity.

$$\begin{aligned} \text{or} \quad & -\log K_w = -\log[\text{H}^+] - \log[\text{OH}^-] \\ \text{Thus} \quad & \text{p}K_w = \text{pH} + \text{pOH} \end{aligned} \quad (14.3)$$

$$\text{Since } K_w = 1.0 \times 10^{-14},$$

$$\text{p}K_w = -\log(1.0 \times 10^{-14}) = 14.00$$

Thus, for *any* aqueous solution at 25°C, pH and pOH add up to 14.00:

$$\text{pH} + \text{pOH} = 14.00 \quad (14.4)$$

SAMPLE EXERCISE 14.6

Calculating pH

The pH of a sample of human blood was measured to be 7.41 at 25°C. Calculate pOH, $[\text{H}^+]$, and $[\text{OH}^-]$ for the sample.

SOLUTION

Since $\text{pH} + \text{pOH} = 14.00$,

$$\text{pOH} = 14.00 - \text{pH} = 14.00 - 7.41 = 6.59$$

To find $[\text{H}^+]$ we must go back to the definition of pH:

$$\text{pH} = -\log[\text{H}^+]$$

Thus

$$7.41 = -\log[\text{H}^+] \quad \text{or} \quad \log[\text{H}^+] = -7.41$$

We need to know the *antilog* of -7.41 . As shown in Appendix 1.2, taking the antilog is the same as exponentiation; that is,

$$\text{antilog}(n) = 10^n$$

Since $\text{pH} = -\log[\text{H}^+]$,

$$-\text{pH} = \log[\text{H}^+]$$

and $[\text{H}^+]$ can be calculated by taking the antilog of $-\text{pH}$:

$$[\text{H}^+] = \text{antilog}(-\text{pH})$$

In the present case,

$$[\text{H}^+] = \text{antilog}(-\text{pH}) = \text{antilog}(-7.41) = 10^{-7.41} = 3.9 \times 10^{-8}$$

Similarly, $[\text{OH}^-] = \text{antilog}(-\text{pOH})$, and

$$[\text{OH}^-] = \text{antilog}(-6.59) = 10^{-6.59} = 2.6 \times 10^{-7} M$$

See Exercises 14.44 through 14.46.

Now that we have considered all the fundamental definitions relevant to acid–base solutions, we can proceed to a quantitative description of the equilibria present in these solutions. The main reason that acid–base problems sometimes seem difficult is that a typical aqueous solution contains many components, so the problems tend to be complicated. However, you can deal with these problems successfully if you use the following general strategies:

- *Think chemistry.* Focus on the solution components and their reactions. It will almost always be possible to choose one reaction that is the most important.
- *Be systematic.* Acid–base problems require a step-by-step approach.
- *Be flexible.* Although all acid–base problems are similar in many ways, important differences do occur. Treat each problem as a separate entity. Do not try to force a given problem into matching any you have solved before. Look for both the similarities and the differences.
- *Be patient.* The complete solution to a complicated problem cannot be seen immediately in all its detail. Pick the problem apart into its workable steps.
- *Be confident.* Look within the problem for the solution, and let the problem guide you. Assume that you can think it out. Do not rely on memorizing solutions to problems. In fact, memorizing solutions is usually detrimental because you tend to try to force a new problem to be the same as one you have seen before. *Understand and think; don't just memorize.*

14.4 Calculating the pH of Strong Acid Solutions

Common Strong Acids

HCl(aq)
HNO₃(aq)
H₂SO₄(aq)
HClO₄(aq)

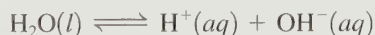
Always write the major species present in the solution.

The H⁺ from the strong acid drives the equilibrium $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$ to the left.

When we deal with acid–base equilibria, we must focus on the solution components and their chemistry. For example, what species are present in a 1.0 M solution of HCl? Since hydrochloric acid is a strong acid, we assume that it is completely dissociated. Thus, although the label on the bottle says 1.0 M HCl, the solution contains virtually no HCl molecules. Typically, container labels indicate the substance(s) used to make up the solution but do not necessarily describe the solution components after dissolution. Thus a 1.0 M HCl solution contains H⁺ and Cl[−] ions rather than HCl molecules.

The next step in dealing with aqueous solutions is to determine which components are significant and which can be ignored. We need to focus on the **major species**, those solution components present in relatively large amounts. In 1.0 M HCl, for example, the major species are H⁺, Cl[−], and H₂O. Since this is a very acidic solution, OH[−] is present only in tiny amounts and is classified as a minor species. In attacking acid–base problems, the importance of *writing the major species in the solution* as the first step cannot be overemphasized. *This single step is the key to solving these problems successfully.*

To illustrate the main ideas involved, let us calculate the pH of 1.0 M HCl. We first list the major species: H⁺, Cl[−], and H₂O. Since we want to calculate the pH, we will focus on those major species that can furnish H⁺. Obviously, we must consider H⁺ from the dissociation of HCl. However, H₂O also furnishes H⁺ by autoionization, which is often represented by the simple dissociation reaction

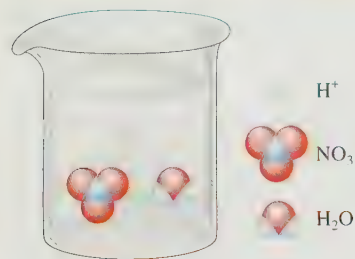


However, is autoionization an important source of H⁺ ions? In pure water at 25°C, [H⁺] is 10^{−7} M. In 1.0 M HCl solution, the water will produce even less than 10^{−7} M H⁺, since by Le Châtelier's principle the H⁺ from the dissociated HCl will drive the position of the water equilibrium to the left. Thus the amount of H⁺ contributed by water is negligible compared with the 1.0 M H⁺ from the dissociation of HCl. Therefore, we can say that [H⁺] in the solution is 1.0 M. The pH is then

$$\text{pH} = -\log[\text{H}^+] = -\log(1.0) = 0$$

SAMPLE EXERCISE 14.7

In pure water, only $10^{-7} M H^+$ is produced.

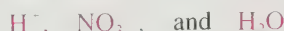


pH of Strong Acids

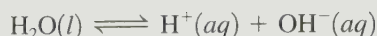
- Calculate the pH of $0.10 M HNO_3$.
- Calculate the pH of $1.0 \times 10^{-10} M HCl$.

SOLUTION

- Since HNO_3 is a strong acid, the major species in solution are



The concentration of HNO_3 is virtually zero, since the acid completely dissociates in water. Also, $[OH^-]$ will be very small because the H^+ ions from the acid will drive the equilibrium



to the left. That is, this is an acidic solution where $[H^+] \gg [OH^-]$, so $[OH^-] \ll 10^{-7} M$. The sources of H^+ are

- H^+ from HNO_3 ($0.10 M$)
- H^+ from H_2O

The number of H^+ ions contributed by the autoionization of water will be very small compared with the $0.10 M$ contributed by the HNO_3 and can be neglected. Since the dissolved HNO_3 is the only important source of H^+ ions in this solution,

$$[H^+] = 0.10 M \quad \text{and} \quad pH = -\log(0.10) = 1.00$$

- Normally, in an aqueous solution of HCl the major species are H^+ , Cl^- , and H_2O . However, in this case the amount of HCl in solution is so small that it has no effect; the only major species is H_2O . Thus the pH will be that of pure water, or $pH = 7.00$.

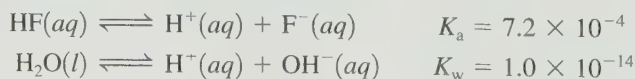
See Exercises 14.47 and 14.48.

14.5 Calculating the pH of Weak Acid Solutions

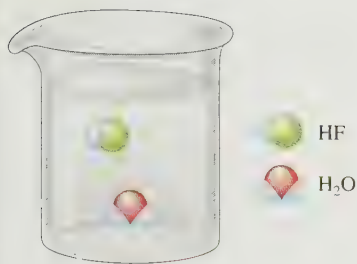
Since a weak acid dissolved in water can be viewed as a prototype of almost any equilibrium occurring in aqueous solution, we will proceed carefully and systematically. Although some of the procedures we develop here may seem unnecessary, they will become essential as the problems become more complicated. We will develop the necessary strategies by calculating the pH of a $1.00 M$ solution of HF ($K_a = 7.2 \times 10^{-4}$).

The first step, as always, is to write the major species in the solution. From its small K_a value, we know that hydrofluoric acid is a weak acid and will be dissociated only to a slight extent. Thus, when we write the major species, the hydrofluoric acid will be represented in its dominant form, as HF . The major species in solution are HF and H_2O .

The next step (since this is a pH problem) is to decide which of the major species can furnish H^+ ions. Actually, both major species can do so:



First, always write the major species present in the solution.



In aqueous solutions, however, typically one source of H^+ can be singled out as dominant. By comparing K_a for HF with K_w for H_2O , we see that hydrofluoric acid, although weak, is still a much stronger acid than water. Thus we will assume that hydrofluoric acid will be the dominant source of H^+ . We will ignore the tiny contribution by water.

Therefore, it is the dissociation of HF that will determine the equilibrium concentration of H^+ and hence the pH:



The equilibrium expression is

$$K_a = 7.2 \times 10^{-4} = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]}$$

To solve the equilibrium problem, we follow the procedures developed in Chapter 13 for gas-phase equilibria. First, we list the initial concentrations, the *concentrations before the reaction of interest has proceeded to equilibrium*. Before any HF dissociates, the concentrations of the species in the equilibrium are

$$[\text{HF}]_0 = 1.00 \text{ M} \quad [\text{F}^-]_0 = 0 \quad [\text{H}^+]_0 = 10^{-7} \text{ M} \approx 0$$

(Note that the zero value for $[\text{H}^+]_0$ is an approximation, since we are neglecting the H^+ ions from the autoionization of water.)

The next step is to determine the change required to reach equilibrium. Since some HF will dissociate to come to equilibrium (but this amount is presently unknown), we let x be the change in the concentration of HF that is required to achieve equilibrium. That is, we assume that x mol/L HF will dissociate to produce x mol/L H^+ and x mol/L F^- as the system adjusts to its equilibrium position. Now the equilibrium concentrations can be defined in terms of x :

$$[\text{HF}] = [\text{HF}]_0 - x = 1.00 - x$$

$$[\text{F}^-] = [\text{F}^-]_0 + x = 0 + x = x$$

$$[\text{H}^+] = [\text{H}^+]_0 + x \approx 0 + x = x$$

Substituting these equilibrium concentrations into the equilibrium expression gives

$$K_a = 7.2 \times 10^{-4} = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]} = \frac{(x)(x)}{1.00 - x}$$

This expression produces a quadratic equation that can be solved using the quadratic formula, as for the gas-phase systems in Chapter 13. However, since K_a for HF is so small, HF will dissociate only slightly, and x is expected to be small. This will allow us to simplify the calculation. If x is very small compared to 1.00, the term in the denominator can be approximated as follows:

$$1.00 - x \approx 1.00$$

The equilibrium expression then becomes

$$7.2 \times 10^{-4} = \frac{(x)(x)}{1.00 - x} \approx \frac{(x)(x)}{1.00}$$

which yields

$$x^2 \approx (7.2 \times 10^{-4})(1.00) = 7.2 \times 10^{-4}$$

$$x \approx \sqrt{7.2 \times 10^{-4}} = 2.7 \times 10^{-2}$$

The validity of an approximation should always be checked.

How valid is the approximation that $[\text{HF}] = 1.00 \text{ M}$? Because this question will arise often in connection with acid–base equilibrium calculations, we will consider it carefully. *The validity of the approximation depends on how much accuracy we demand for the calculated value of $[\text{H}^+]$.* Typically, the K_a values for acids are known to an accuracy of only about $\pm 5\%$. It is reasonable therefore to apply this figure when determining the validity of the approximation

$$[\text{HA}]_0 - x \approx [\text{HA}]_0$$

We will use the following test. First, we calculate the value of x by making the approximation

$$K_a = \frac{x^2}{[\text{HA}]_0 - x} \approx \frac{x^2}{[\text{HA}]_0}$$

where $x^2 \approx K_a[\text{HA}]_0$ and $x \approx \sqrt{K_a[\text{HA}]_0}$

We then compare the sizes of x and $[\text{HA}]_0$. If the expression

$$\frac{x}{[\text{HA}]_0} \times 100\%$$

is less than or equal to 5%, the value of x is small enough that the approximation

$$[\text{HA}]_0 - x \approx [\text{HA}]_0$$

will be considered valid.

In our example,

$$x = 2.7 \times 10^{-2} \text{ mol/L}$$

$$[\text{HA}]_0 = [\text{HF}]_0 = 1.00 \text{ mol/L}$$

$$\text{and } \frac{x}{[\text{HA}]_0} \times 100 = \frac{2.7 \times 10^{-2}}{1.00} \times 100\% = 2.7\%$$

The approximation we made is considered valid, and the value of x calculated using that approximation is acceptable. Thus

$$x = [\text{H}^+] = 2.7 \times 10^{-2} \text{ M} \quad \text{and} \quad \text{pH} = -\log(2.7 \times 10^{-2}) = 1.57$$

This problem illustrates all the important steps for solving a typical equilibrium problem involving a weak acid. These steps are summarized as follows:

Solving Weak Acid Equilibrium Problems

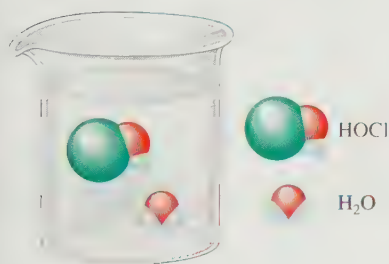
- ➡ **1** List the major species in the solution.
- ➡ **2** Choose the species that can produce H^+ , and write balanced equations for the reactions producing H^+ .
- ➡ **3** Using the values of the equilibrium constants for the reactions you have written, decide which equilibrium will dominate in producing H^+ .
- ➡ **4** Write the equilibrium expression for the dominant equilibrium.

The K_a values for various weak acids are given in Table 14.2 and in Appendix 5.1.

- ➡ **5** List the initial concentrations of the species participating in the dominant equilibrium.
- ➡ **6** Define the change needed to achieve equilibrium; that is, define x .
- ➡ **7** Write the equilibrium concentrations in terms of x .
- ➡ **8** Substitute the equilibrium concentrations into the equilibrium expression.
- ➡ **9** Solve for x the “easy” way, that is, by assuming that $[HA]_0 - x \approx [HA]_0$.
- ➡ **10** Use the 5% rule to verify whether the approximation is valid.
- ➡ **11** Calculate $[H^+]$ and pH.

We use this systematic approach in Sample Exercise 14.8.

SAMPLE EXERCISE 14.8



The pH of Weak Acids

The hypochlorite ion (OCI^-) is a strong oxidizing agent often found in household bleaches and disinfectants. It is also the active ingredient that forms when swimming pool water is treated with chlorine. In addition to its oxidizing abilities, the hypochlorite ion has a relatively high affinity for protons (it is a much stronger base than Cl^- , for example) and forms the weakly acidic hypochlorous acid ($HOCl$, $K_a = 3.5 \times 10^{-8}$). Calculate the pH of a 0.100 M aqueous solution of hypochlorous acid.

SOLUTION

- ➡ **1** We list the major species. Since $HOCl$ is a weak acid and remains mostly undissociated, the major species in a 0.100 M $HOCl$ solution are



- ➡ **2** Both species can produce H^+ :



- ➡ **3** Since $HOCl$ is a significantly stronger acid than H_2O , it will dominate in the production of H^+ .

- ➡ **4** We therefore use the following equilibrium expression:

$$K_a = 3.5 \times 10^{-8} = \frac{[H^+][OCI^-]}{[HOCl]}$$

- ➡ **5** The initial concentrations appropriate for this equilibrium are

$$[HOCl]_0 = 0.100 \, M$$

$$[OCI^-]_0 = 0$$

$$[H^+]_0 \approx 0 \quad (\text{We neglect the contribution from } H_2O.)$$

- ➡ **6** Since the system will reach equilibrium by the dissociation of $HOCl$, let x be the amount of $HOCl$ (in mol/L) that dissociates in reaching equilibrium.

- ➡ **7** The equilibrium concentrations in terms of x are

$$[HOCl] = [HOCl]_0 - x = 0.100 - x$$

$$[OCI^-] = [OCI^-]_0 + x = 0 + x = x$$

$$[H^+] = [H^+]_0 + x \approx 0 + x = x$$



Swimming pool water must be frequently tested for pH and chlorine content.

➡ **8** Substituting these concentrations into the equilibrium expression gives

$$K_a = 3.5 \times 10^{-8} = \frac{(x)(x)}{0.100 - x}$$

➡ **9** Since K_a is so small, we can expect a small value for x . Thus we make the approximation $[HA]_0 - x \approx [HA]_0$, or $0.100 - x \approx 0.100$, which leads to the expression

$$K_a = 3.5 \times 10^{-8} = \frac{x^2}{0.100 - x} \approx \frac{x^2}{0.100}$$

Solving for x gives

$$x = 5.9 \times 10^{-5}$$

➡ **10** The approximation $0.100 - x \approx 0.100$ must be validated. To do this, we compare x to $[HOCl]_0$:

$$\frac{x}{[HA]_0} \times 100 = \frac{x}{[HOCl]_0} \times 100 = \frac{5.9 \times 10^{-5}}{0.100} \times 100 = 0.059\%$$

Since this value is much less than 5%, the approximation is considered valid.

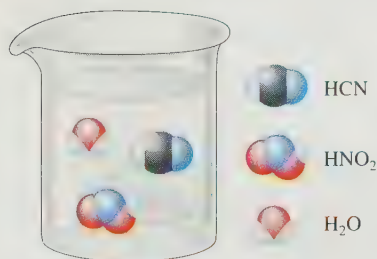
➡ **11** We calculate $[H^+]$ and pH:

$$[H^+] = x = 5.9 \times 10^{-5} M \quad \text{and} \quad \text{pH} = 4.23$$

See Exercises 14.53 through 14.55.

The same systematic approach applies to all solution equilibria.

SAMPLE EXERCISE 14.9



The pH of a Mixture of Weak Acids

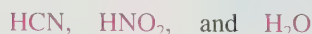
Sometimes a solution contains two weak acids of very different strengths. This case is considered in Sample Exercise 14.9. Note that the steps are again followed (though not labeled).

The pH of Weak Acid Mixtures

Calculate the pH of a solution that contains 1.00 M HCN ($K_a = 6.2 \times 10^{-10}$) and 5.00 M HNO_2 ($K_a = 4.0 \times 10^{-4}$). Also calculate the concentration of cyanide ion (CN^-) in this solution at equilibrium.

SOLUTION

Since HCN and HNO_2 are both weak acids and are largely undissociated, the major species in the solution are:



All three of these components produce H^+ :



A mixture of three acids might lead to a very complicated problem. However, the situation is greatly simplified by the fact that even though HNO_2 is a weak acid, it is much stronger than the other two acids present (as revealed by the K values). Thus

HNO_2 can be assumed to be the dominant producer of H^+ , and we will focus on the equilibrium expression

$$K_a = 4.0 \times 10^{-4} = \frac{[\text{H}^+][\text{NO}_2^-]}{[\text{HNO}_2]}$$

The initial concentrations, the definition of x , and the equilibrium concentrations are as follows:

Initial Concentration (mol/L)		Equilibrium Concentration (mol/L)
$[\text{HNO}_2]_0 = 5.00$	$\xrightarrow[\text{dissociates}]{x \text{ mol/L } \text{HNO}_2}$	$[\text{HNO}_2] = 5.00 - x$
$[\text{NO}_2^-]_0 = 0$		$[\text{NO}_2^-] = x$
$[\text{H}^+]_0 \approx 0$		$[\text{H}^+] = x$

It is convenient to represent these concentrations in the following shorthand form (called an ICE table):

	$\text{HNO}_2(aq)$	$\rightleftharpoons$	$\text{H}^+(aq)$	+	$\text{NO}_2^-(aq)$
Initial:	5.00		0		0
Change:	$-x$		$+x$		$+x$
Equilibrium:	$5.00 - x$		x		x

Substituting the equilibrium concentrations in the equilibrium expression and making the approximation that $5.00 - x = 5.00$ give

$$K_a = 4.0 \times 10^{-4} = \frac{(x)(x)}{5.00 - x} \approx \frac{x^2}{5.00}$$

We solve for x :

$$x = 4.5 \times 10^{-2}$$

Using the 5% rule, we show that the approximation is valid:

$$\frac{x}{[\text{HNO}_2]_0} \times 100 = \frac{4.5 \times 10^{-2}}{5.00} \times 100 = 0.90\%$$

Therefore,

$$[\text{H}^+] = x = 4.5 \times 10^{-2} M \quad \text{and} \quad \text{pH} = 1.35$$

We also want to calculate the equilibrium concentration of cyanide ion in this solution. The CN^- ions in this solution come from the dissociation of HCN :



Although the position of this equilibrium lies far to the left and does not contribute *significantly* to $[\text{H}^+]$, HCN is the *only source* of CN^- . Thus we must consider the extent of the dissociation of HCN to calculate $[\text{CN}^-]$. The equilibrium expression for the preceding reaction is

$$K_a = 6.2 \times 10^{-10} = \frac{[\text{H}^+][\text{CN}^-]}{[\text{HCN}]}$$

We know $[H^+]$ for this solution from the results of the first part of the problem. It is important to understand that *there is only one kind of H^+ in this solution*. It does not matter from which acid the H^+ ions originate. The equilibrium $[H^+]$ we need to insert into the HCN equilibrium expression is $4.5 \times 10^{-2} M$, even though the H^+ was contributed almost entirely from the dissociation of HNO_2 . What is $[HCN]$ at equilibrium? We know $[HCN]_0 = 1.00 M$, and since K_a for HCN is so small, a negligible amount of HCN will dissociate. Thus

$$[HCN] = [HCN]_0 - \text{amount of HCN dissociated} \approx [HCN]_0 = 1.00 M$$

Since $[H^+]$ and $[HCN]$ are known, we can find $[CN^-]$ from the equilibrium expression:

$$K_a = 6.2 \times 10^{-10} = \frac{[H^+][CN^-]}{[HCN]} = \frac{(4.5 \times 10^{-2})[CN^-]}{1.00}$$

$$[CN^-] = \frac{(6.2 \times 10^{-10})(1.00)}{4.5 \times 10^{-2}} = 1.4 \times 10^{-8} M$$

Note the significance of this result. Since $[CN^-] = 1.4 \times 10^{-8} M$ and HCN is the only source of CN^- , this means that only $1.4 \times 10^{-8} \text{ mol/L}$ of HCN dissociated. This is a very small amount compared with the initial concentration of HCN, which is exactly what we would expect from its very small K_a value, and $[HCN] = 1.00 M$ as assumed.

See Exercises 14.61 and 14.62.

Percent Dissociation

Percent dissociation is also known as percent ionization.

It is often useful to specify the amount of weak acid that has dissociated in achieving equilibrium in an aqueous solution. The **percent dissociation** is defined as follows:

$$\text{Percent dissociation} = \frac{\text{amount dissociated (mol/L)}}{\text{initial concentration (mol/L)}} \times 100\% \quad (14.5)$$

For example, we found earlier that in a $1.00 M$ solution of HF, $[H^+] = 2.7 \times 10^{-2} M$. To reach equilibrium, $2.7 \times 10^{-2} \text{ mol/L}$ of the original $1.00 M$ HF dissociates, so

$$\text{Percent dissociation} = \frac{2.7 \times 10^{-2} \text{ mol/L}}{1.00 \text{ mol/L}} \times 100\% = 2.7\%$$

For a given weak acid, the percent dissociation increases as the acid becomes more dilute. For example, the percent dissociation of acetic acid ($HC_2H_3O_2$, $K_a = 1.8 \times 10^{-5}$) is significantly greater in a $0.10 M$ solution than in a $1.0 M$ solution, as demonstrated in Sample Exercise 14.10.

SAMPLE EXERCISE 14.10

Calculating Percent Dissociation

Calculate the percent dissociation of acetic acid ($K_a = 1.8 \times 10^{-5}$) in each of the following solutions.

- $1.00 M HC_2H_3O_2$
- $0.100 M HC_2H_3O_2$

SOLUTION

- a. Since acetic acid is a weak acid, the major species in this solution are $\text{HC}_2\text{H}_3\text{O}_2$ and H_2O . Both species are weak acids, but acetic acid is a much stronger acid than water. Thus the dominant equilibrium will be



and the equilibrium expression is

$$K_a = 1.8 \times 10^{-5} = \frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]}$$

The initial concentrations, definition of x , and equilibrium concentrations are:

	$\text{HC}_2\text{H}_3\text{O}_2(aq)$	$\rightleftharpoons$	$\text{H}^+(aq)$	+	$\text{C}_2\text{H}_3\text{O}_2^-(aq)$
Initial:	1.00		0		0
Change:	$-x$		x		x
Equilibrium:	$1.00 - x$		x		x

Inserting the equilibrium concentrations into the equilibrium expression and making the usual approximation that x is small compared with $[\text{HA}]_0$ give

$$K_a = 1.8 \times 10^{-5} = \frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = \frac{(x)(x)}{1.00 - x} \approx \frac{x^2}{1.00}$$

Thus

$$x^2 \approx 1.8 \times 10^{-5} \quad \text{and} \quad x \approx 4.2 \times 10^{-3}$$

The approximation $1.00 - x \approx 1.00$ is valid by the 5% rule (check this yourself), so

$$[\text{H}^+] = x = 4.2 \times 10^{-3} M$$

The percent dissociation is

$$\frac{[\text{H}^+]}{[\text{HC}_2\text{H}_3\text{O}_2]_0} \times 100 = \frac{4.2 \times 10^{-3}}{1.00} \times 100\% = 0.42\%$$

- b. This is a similar problem, except that in this case $[\text{HC}_2\text{H}_3\text{O}_2] = 0.100 M$. Analysis of the problem leads to the expression

$$K_a = 1.8 \times 10^{-5} = \frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = \frac{(x)(x)}{0.100 - x} \approx \frac{x^2}{0.100}$$

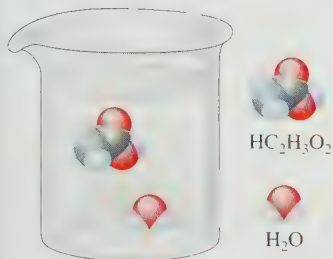
Thus

$$x = [\text{H}^+] = 1.3 \times 10^{-3} M$$

and

$$\text{Percent dissociation} = \frac{1.3 \times 10^{-3}}{0.10} \times 100\% = 1.3\%$$

See Exercises 14.63 and 14.64.



An acetic acid solution, which is a weak electrolyte, contains only a few ions and does not conduct as much current as a strong electrolyte. The bulb is only dimly lit.

The results in Sample Exercise 14.10 show two important facts. The concentration of H^+ ion at equilibrium is smaller in the $0.10 M$ acetic acid solution than in the $1.0 M$ acetic acid solution, as we would expect. However, the percent

CHEMICAL IMPACT

Household Chemistry

Common household bleach is an aqueous solution containing approximately 5% sodium hypochlorite, a potent oxidizing agent that can react with and decolorize chemicals that cause stains. Bleaching solutions are manufactured by dissolving chlorine gas in a sodium hydroxide solution to give the reaction



As long as the pH of this solution is maintained above 8, the OCl^- ion is the predominant chlorine-containing species. However, if the solution is made acidic (the $[\text{OH}^-]$ lowered), elemental chlorine (Cl_2) is favored, and since Cl_2 is much less soluble in water than is sodium hypochlorite, Cl_2 gas is suddenly evolved from the solution. This is why labels on bottles of bleach carry warnings about mixing the bleach with other cleaning solutions. For example, toilet bowl cleaners usually contain acids such as H_3PO_4 or HSO_4^- and have pH values around 2. Mixing toilet bowl cleaner with bleach can lead to a very dangerous evolution of chlorine gas.

On the other hand, if bleach is mixed with a cleaning agent containing ammonia, the chlorine and ammonia react to produce chloramines, such as NH_2Cl , NHCl_2 , and NCl_3 . These compounds produce acrid fumes that can cause respiratory distress.

HOUSEHOLD USE

Toilet bowls. Flush toilet. Pour 1 cup of bleach into bowl. Brush. Let stand 10 minutes before flushing again.

Kitchen sinks. Cover stains with 1 gallon of water before adding 2/3 cup of Safeway Regular Ultra Bleach. Let stand 5 minutes before rinsing.

Bathtubs and showers, floors, vinyl, tile, woodwork and appliances. Clean with a solution of 2/3 cup of bleach per gallon of warm water. Let stand 5 minutes before rinsing.

DANGER: CORROSIVE.

Contains Sodium Hypochlorite
Contains No Phosphates

Causes substantial but temporary eye injury. Avoid contact with eyes or on clothing. Harmful if swallowed. May irritate skin. For prolonged use, wear gloves.

Treatment: If in eyes rinse with plenty of water for 15 minutes. If swallowed, drink a glassful of water. Call physician or Poison Control Center in either case. If in contact with skin wash skin thoroughly with soap and water.

Add only to water, do not mix with acid or other household chemicals such as toilet bowl cleaners, ammonia or rust removers. To do so may release hazardous gases. Prolonged contact with metal may cause pitting or discoloration.

Storage and disposal: Store in a cool dry area, away from direct sunlight and heat to avoid deterioration. Do not reuse empty container; instead, rinse and put in trash collection.

The label on this bleach bottle warns of the hazards of mixing cleaning solutions.

The more dilute the weak acid solution, the greater is the percent dissociation.

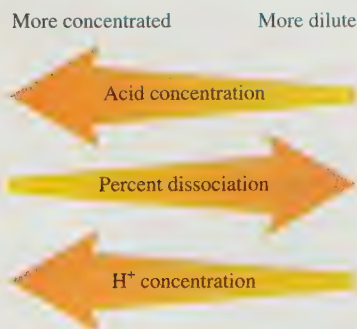


FIGURE 14.10

The effect of dilution on the percent dissociation and $[\text{H}^+]$ of a weak acid solution.

dissociation is significantly greater in the 0.10 M solution than in the 1.0 M solution. This is a general result. For solutions of any weak acid HA, $[\text{H}^+]$ decreases as $[\text{HA}]_0$ decreases, but the percent dissociation increases as $[\text{HA}]_0$ decreases. This phenomenon can be explained as follows.

Consider the weak acid HA with the initial concentration $[\text{HA}]_0$, where at equilibrium

$$[\text{HA}] = [\text{HA}]_0 - x \approx [\text{HA}]_0$$

$$[\text{H}^+] = [\text{A}^-] = x$$

Thus

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \approx \frac{(x)(x)}{[\text{HA}]_0}$$

Now suppose enough water is added suddenly to dilute the solution by a factor of 10. The new concentrations before any adjustment occurs are

$$[\text{A}^-]_{\text{new}} = [\text{H}^+]_{\text{new}} = \frac{x}{10}$$

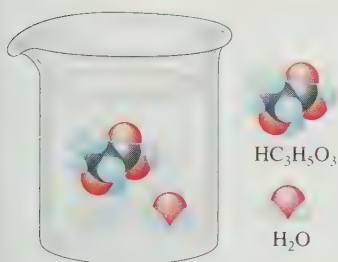
$$[\text{HA}]_{\text{new}} = \frac{[\text{HA}]_0}{10}$$

and Q , the reaction quotient, is

$$Q = \frac{\left(\frac{x}{10}\right)\left(\frac{x}{10}\right)}{\frac{[HA]_0}{10}} = \frac{1(x)(x)}{10[HA]_0} = \frac{1}{10}K_a$$

Since Q is less than K_a , the system must adjust to the right to reach the new equilibrium position. Thus the percent dissociation increases when the acid is diluted. This behavior is summarized in Fig. 14.10. In Sample Exercise 14.11 we see how the percent dissociation can be used to calculate the K_a value for a weak acid.

SAMPLE EXERCISE 14.11

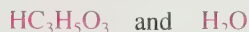


Calculating K_a from Percent Dissociation

Lactic acid (HC₃H₅O₃) is a waste product that accumulates in muscle tissue during exertion, leading to pain and a feeling of fatigue. In a 0.100 M aqueous solution, lactic acid is 3.7% dissociated. Calculate the value of K_a for this acid.

SOLUTION

From the small value for the percent dissociation, it is clear that HC₃H₅O₃ is a weak acid. Thus the major species in the solution are the undissociated acid and water:



However, even though HC₃H₅O₃ is a weak acid, it is a much stronger acid than water and will be the dominant source of H⁺ in the solution. The dissociation reaction is



and the equilibrium expression is

$$K_a = \frac{[\text{H}^+][\text{C}_3\text{H}_5\text{O}_3^-]}{[\text{HC}_3\text{H}_5\text{O}_3]}$$

The initial and equilibrium concentrations are as follows:

Initial Concentration		Equilibrium Concentration
$[\text{HC}_3\text{H}_5\text{O}_3]_0 = 0.10 \text{ M}$	$\xrightarrow[\text{dissociates}]{\text{HC}_3\text{H}_5\text{O}_3}$	$[\text{HC}_3\text{H}_5\text{O}_3] = 0.10 - x$
$[\text{C}_3\text{H}_5\text{O}_3^-]_0 = 0$		$[\text{C}_3\text{H}_5\text{O}_3^-] = x$
$[\text{H}^+]_0 \approx 0$		$[\text{H}^+] = x$

The change needed to reach equilibrium can be obtained from the percent dissociation and Equation (14.5). For this acid,

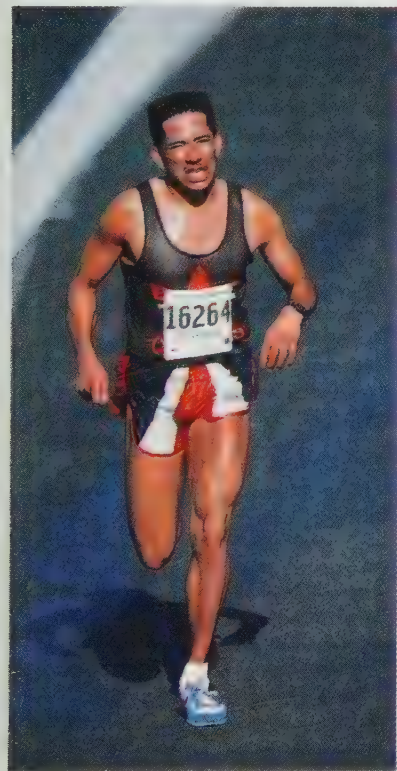
$$\text{Percent dissociation} = 3.7\% = \frac{x}{[\text{HC}_3\text{H}_5\text{O}_3]_0} \times 100\% = \frac{x}{0.10} \times 100\%$$

and

$$x = \frac{3.7}{100}(0.10) = 3.7 \times 10^{-3} \text{ mol/L}$$

Now we can calculate the equilibrium concentrations:

$$\begin{aligned} [\text{HC}_3\text{H}_5\text{O}_3] &= 0.10 - x = 0.10 \text{ M} \quad (\text{to the correct number of significant figures}) \\ [\text{C}_3\text{H}_5\text{O}_3^-] &= [\text{H}^+] = x = 3.7 \times 10^{-3} \text{ M} \end{aligned}$$



Strenuous exercise causes a buildup of lactic acid in muscle tissues.

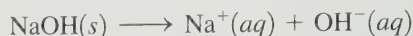
These concentrations can now be used to calculate the value of K_a for lactic acid:

$$K_a = \frac{[\text{H}^+][\text{C}_3\text{H}_5\text{O}_3^-]}{[\text{HC}_3\text{H}_5\text{O}_3]} = \frac{(3.7 \times 10^{-3})(3.7 \times 10^{-3})}{0.10} = 1.4 \times 10^{-4}$$

See Exercises 14.65 and 14.66.

14.6 Bases

According to the Arrhenius concept, a base is a substance that produces OH^- ions in aqueous solution. According to the Brønsted–Lowry model, a base is a proton acceptor. The bases sodium hydroxide (NaOH) and potassium hydroxide (KOH) fulfill both criteria. They contain OH^- ions in the solid lattice and, behaving as strong electrolytes, dissociate completely when dissolved in aqueous solution:

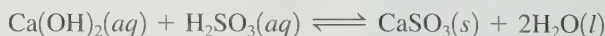
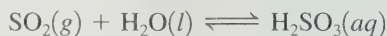


leaving virtually no undissociated NaOH . Thus a 1.0 M NaOH solution really contains 1.0 M Na^+ and 1.0 M OH^- . Because of their complete dissociation, NaOH and KOH are called **strong bases** in the same sense as we defined strong acids.

All the hydroxides of the Group 1A elements (LiOH , NaOH , KOH , RbOH , and CsOH) are strong bases, but only NaOH and KOH are common laboratory reagents, because the lithium, rubidium, and cesium compounds are expensive. The alkaline earth (Group 2A) hydroxides— $\text{Ca}(\text{OH})_2$, $\text{Ba}(\text{OH})_2$, and $\text{Sr}(\text{OH})_2$ —are also strong bases. For these compounds, two moles of hydroxide ion are produced for every mole of metal hydroxide dissolved in aqueous solution.

The alkaline earth hydroxides are not very soluble and are used only when the solubility factor is not important. In fact, the low solubility of these bases can sometimes be an advantage. For example, many antacids are suspensions of metal hydroxides, such as aluminum hydroxide and magnesium hydroxide. The low solubility of these compounds prevents a large hydroxide ion concentration that would harm the tissues of the mouth, esophagus, and stomach. Yet these suspensions furnish plenty of hydroxide ion to react with the stomach acid, since the salts dissolve as this reaction proceeds.

Calcium hydroxide, $\text{Ca}(\text{OH})_2$, often called **slaked lime**, is widely used in industry because it is inexpensive and plentiful. For example, slaked lime is used in scrubbing stack gases to remove sulfur dioxide from the exhaust of power plants and factories. In the scrubbing process a suspension of slaked lime is sprayed into the stack gases to react with sulfur dioxide gas according to the following steps:



Slaked lime is also widely used in water treatment plants for softening hard water, which involves the removal of ions, such as Ca^{2+} and Mg^{2+} , that hamper the action of detergents. The softening method most often employed in water treatment plants is the **lime–soda process**, in which **lime** (CaO) and **soda ash** (Na_2CO_3) are added to the water. As we will see in more detail later in this chapter, the CO_3^{2-} ion reacts with water to produce the HCO_3^- ion. When the lime is added to the water, it forms slaked lime, that is,



In a basic solution at 25°C, $\text{pH} > 7$.



Visualization: Limewater

Drug Facts

Active ingredients (in each tsp=5 mL)

Active ingredients	Purpose
Aluminum hydroxide (equiv. to dried gel, USP) 200 mg	Antacid
Magnesium hydroxide 200 mg	Antacid
Simethicone 20 mg	Antigas

Uses relieves ■ heartburn ■ sour stomach ■ gas
■ acid indigestion ■ upset stomach due to these symptoms

Warnings
Ask a doctor before use if you have kidney disease
Ask a doctor or pharmacist before use if you are presently taking a prescription drug. Antacids may interact with certain prescription drugs.
When using this product do not exceed 24 tsp (120 mL) in a 24-hour period or use the maximum dosage for more than 2 weeks.
Stop use and ask a doctor if symptoms last for more than 2 weeks.
If pregnant or breast-feeding, ask a health professional before use.
Keep out of reach of children.

Directions ■ shake well before use
■ take 2-4 tsp (10-20 mL) between meals and at bedtime

Inactive ingredients butylparaben, carboxymethylcellulose sodium, FD&C red #40, flavor, hydroxypropyl methylcellulose, microcrystalline cellulose, propylparaben, purified water, saccharin sodium, sorbitol

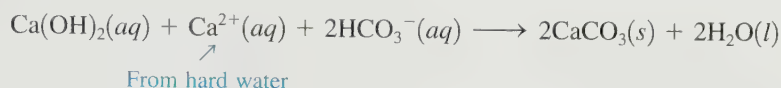
Questions or comments?
1-800-842-7886

Store at room temperature tightly closed.

An antacid containing aluminum and magnesium hydroxides.

Calcium carbonate is also used in scrubbing, as discussed in Section 5.9.

which then reacts with the HCO_3^- ion from the added soda ash and a Ca^{2+} ion in the hard water to produce calcium carbonate:



Thus, for every mole of Ca(OH)_2 consumed, 1 mole of Ca^{2+} is removed from the hard water, thereby softening it. Some hard water naturally contains bicarbonate ions. In this case, no soda ash is needed—simply adding the lime produces the softening.

Calculating the pH of a strong base solution is relatively simple, as illustrated in Sample Exercise 14.12.

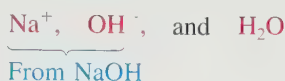
SAMPLE EXERCISE 14.12

The pH of Strong Bases

Calculate the pH of a $5.0 \times 10^{-2} \text{ M}$ NaOH solution.

SOLUTION

The major species in this solution are



Although autoionization of water also produces OH^- ions, the pH will be dominated by the OH^- ions from the dissolved NaOH. Thus, in the solution,

$$[\text{OH}^-] = 5.0 \times 10^{-2} \text{ M}$$

and the concentration of H^+ can be calculated from K_w :

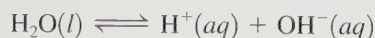
$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{5.0 \times 10^{-2}} = 2.0 \times 10^{-13} \text{ M}$$

$$\text{pH} = 12.70$$

Note that this is a basic solution for which

$$[\text{OH}^-] > [\text{H}^+] \quad \text{and} \quad \text{pH} > 7$$

The added OH^- from the salt has shifted the water autoionization equilibrium

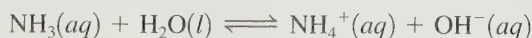


to the left, significantly lowering $[\text{H}^+]$ compared with that in pure water.

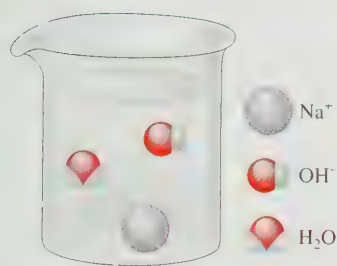
See Exercises 14.77 through 14.80.

A base does not have to contain hydroxide ion.

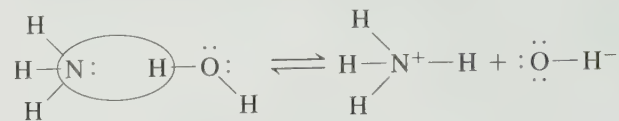
Many types of proton acceptors (bases) do not contain the hydroxide ion. However, when dissolved in water, these substances increase the concentration of hydroxide ion because of their reaction with water. For example, ammonia reacts with water as follows:



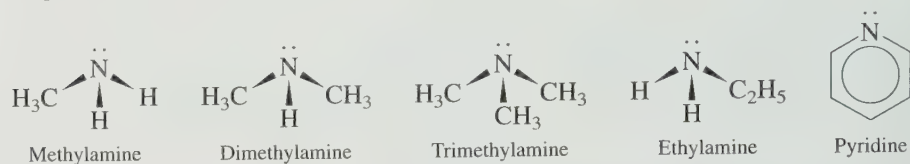
The ammonia molecule accepts a proton and thus functions as a base. Water is the acid in this reaction. Note that even though the base ammonia contains no hydroxide ion, it still increases the concentration of hydroxide ion to yield a basic solution.



Bases such as ammonia typically have at least one unshared pair of electrons that is capable of forming a bond with a proton. The reaction of an ammonia molecule with a water molecule can be represented as follows:



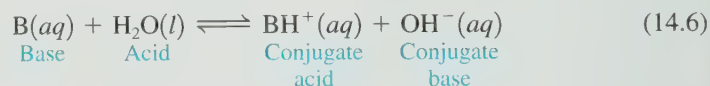
There are many bases like ammonia that produce hydroxide ion by reaction with water. In most of these bases, the lone pair is located on a nitrogen atom. Some examples are



Note that the first four bases can be thought of as substituted ammonia molecules with hydrogen atoms replaced by methyl (CH_3) or ethyl (C_2H_5) groups. The pyridine molecule is like benzene



except that a nitrogen atom replaces one of the carbon atoms in the ring. The general reaction between a base B and water is given by



The equilibrium constant for this general reaction is

$$K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]}$$

Appendix 5.3 contains a table of K_b values.

where K_b always refers to the reaction of a base with water to form the conjugate acid and the hydroxide ion.

Bases of the type represented by B in Equation (14.6) compete with OH^- , a very strong base, for the H^+ ion. Thus their K_b values tend to be small (for example, for ammonia, $K_b = 1.8 \times 10^{-5}$), and they are called **weak bases**. The values of K_b for some common weak bases are listed in Table 14.3.

TABLE 14.3 Values of K_b for Some Common Weak Bases

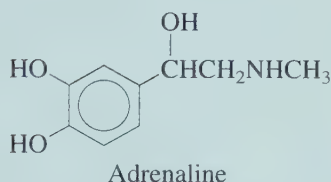
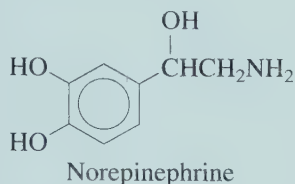
Name	Formula	Conjugate Acid	K_b
Ammonia	NH_3	NH_4^+	1.8×10^{-5}
Methylamine	CH_3NH_2	CH_3NH_3^+	4.38×10^{-4}
Ethylamine	$\text{C}_2\text{H}_5\text{NH}_2$	$\text{C}_2\text{H}_5\text{NH}_3^+$	5.6×10^{-4}
Aniline	$\text{C}_6\text{H}_5\text{NH}_2$	$\text{C}_6\text{H}_5\text{NH}_3^+$	3.8×10^{-10}
Pyridine	$\text{C}_5\text{H}_5\text{N}$	$\text{C}_5\text{H}_5\text{NH}^+$	1.7×10^{-9}



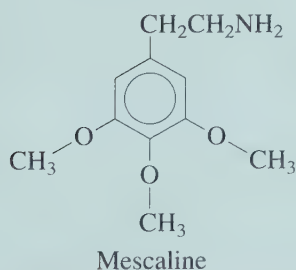
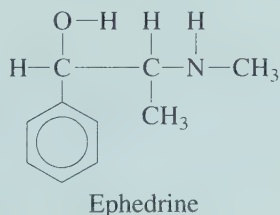
CHEMICAL IMPACT

Amines

We have seen that many bases have nitrogen atoms with one lone pair and can be viewed as substituted ammonia molecules, with the general formula $R_xNH_{(3-x)}$. Compounds of this type are called **amines**. Amines are widely distributed in animals and plants, and complex amines often serve as messengers or regulators. For example, in the human nervous system, there are two amine stimulants, *norepinephrine* and *adrenaline*.

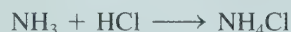


Ephedrine, widely used as a decongestant, was a known drug in China over 2000 years ago. Indians in Mexico and the Southwest have used the hallucinogen *mescaline*, extracted from the peyote cactus, for centuries.

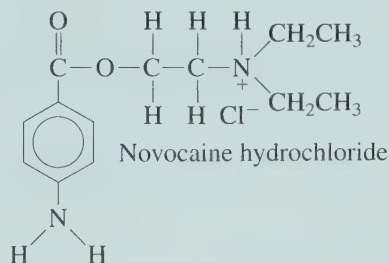


Peyote cactus growing on a rock.

Many other drugs, such as codeine and quinine, are amines, but they are usually not used in their pure amine forms. Instead, they are treated with an acid to become acid salts. An example of an acid salt is ammonium chloride, obtained by the reaction



Amines also can be protonated in this way. The resulting acid salt, written as $AHCl$ (where A represents the amine), contains AH^+ and Cl^- . In general, the acid salts are more stable and more soluble in water than the parent amines. For instance, the parent amine of the well-known local anesthetic *novocaine* is insoluble in water, whereas the acid salt is much more soluble.



Typically, pH calculations for solutions of weak bases are very similar to those for weak acids, as illustrated by Sample Exercises 14.13 and 14.14.

SAMPLE EXERCISE 14.13

The pH of Weak Bases I

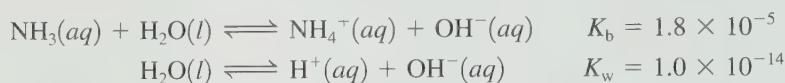
Calculate the pH for a 15.0 *M* solution of NH_3 ($K_b = 1.8 \times 10^{-5}$).

SOLUTION

Since ammonia is a weak base, as can be seen from its small K_b value, most of the dissolved NH_3 will remain as NH_3 . Thus the major species in solution are



Both these substances can produce OH^- according to the reactions



However, the contribution from water can be neglected, since $K_b \gg K_w$. The equilibrium for NH_3 will dominate, and the equilibrium expression to be used is

$$K_b = 1.8 \times 10^{-5} = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

The appropriate concentrations are

Refer to the steps for solving weak acid equilibrium problems. Use the same systematic approach for weak base equilibrium problems.

Initial Concentration (mol/L)		Equilibrium Concentration (mol/L)
$[\text{NH}_3]_0 = 15.0$	$\xrightarrow[\text{H}_2\text{O to reach equilibrium}]{\begin{smallmatrix} x \text{ mol/L} \\ \text{NH}_3 \text{ reacts with} \end{smallmatrix}}$	$[\text{NH}_3] = 15.0 - x$
$[\text{NH}_4^+]_0 = 0$		$[\text{NH}_4^+] = x$
$[\text{OH}^-]_0 \approx 0$		$[\text{OH}^-] = x$

In terms of an ICE table, these concentrations are:

	$\text{NH}_3(\text{aq})$	+	$\text{H}_2\text{O}(\text{l})$	$\rightleftharpoons$	$\text{NH}_4^+(\text{aq})$	+	$\text{OH}^-(\text{aq})$
Initial:	15.0	—			0		0
Change:	$-x$	—			$+x$		$+x$
Equilibrium:	$15.0 - x$	—			x		x

Substituting the equilibrium concentrations into the equilibrium expression and making the usual approximation gives

$$K_b = 1.8 \times 10^{-5} = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{(x)(x)}{15.0 - x} \approx \frac{x^2}{15.0}$$

Thus

$$x \approx 1.6 \times 10^{-2}$$

The 5% rule validates the approximation (check it yourself), so

$$[\text{OH}^-] = 1.6 \times 10^{-2} \text{ M}$$

Since we know that K_w must be satisfied for this solution, we can calculate $[H^+]$ as follows:

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{1.6 \times 10^{-2}} = 6.3 \times 10^{-13} M$$

Therefore, $pH = -\log(6.3 \times 10^{-13}) = 12.20$

See Exercises 14.83 and 14.84.

Sample Exercise 14.13 illustrates how a typical weak base equilibrium problem should be solved. Note two additional important points:

A table of K_b values for bases is also given in Appendix 5.3.

1. We calculated $[H^+]$ from K_w and then calculated the pH, but another method is available. The pOH could have been calculated from $[OH^-]$ and then used in Equation (14.3):

$$\begin{aligned} pK_w &= 14.00 = pH + pOH \\ pH &= 14.00 - pOH \end{aligned}$$

2. In a 15.0 M NH_3 solution, the equilibrium concentrations of NH_4^+ and OH^- are each $1.6 \times 10^{-2} M$. Only a small percentage,

$$\frac{1.6 \times 10^{-2}}{15.0} \times 100\% = 0.11\%$$

of the ammonia reacts with water. Bottles containing 15.0 M NH_3 solution are often labeled 15.0 M NH_4OH , but as you can see from these results, 15.0 M NH_3 is actually a much more accurate description of the solution contents.

SAMPLE EXERCISE 14.14

The pH of Weak Bases II

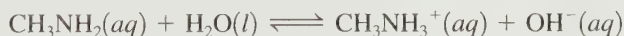
Calculate the pH of a 1.0 M solution of methylamine ($K_b = 4.38 \times 10^{-4}$).

SOLUTION

Since methylamine (CH_3NH_2) is a weak base, the major species in solution are



Both are bases; however, water can be neglected as a source of OH^- , so the dominant equilibrium is

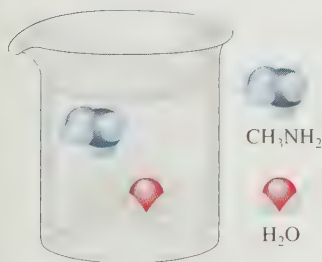


and
$$K_b = 4.38 \times 10^{-4} = \frac{[CH_3NH_3^+][OH^-]}{[CH_3NH_2]}$$

The ICE table is:

	$CH_3NH_2(aq)$	+	$H_2O(l)$	$\rightleftharpoons$	$CH_3NH_3^+(aq)$	+	$OH^-(aq)$
Initial:	1.0		—		0		0
Change:	—x		—		+x		+x
Equilibrium:	1.0 — x		—		x		x

Substituting the equilibrium concentrations in the equilibrium expression and making the usual approximation give



$$K_b = 4.38 \times 10^{-4} = \frac{[\text{CH}_3\text{NH}_3^+][\text{OH}^-]}{[\text{CH}_3\text{NH}_2]} = \frac{(x)(x)}{1.0 - x} \approx \frac{x^2}{1.0}$$

and

$$x \approx 2.1 \times 10^{-2}$$

The approximation is valid by the 5% rule, so

$$[\text{OH}^-] = x = 2.1 \times 10^{-2} M$$

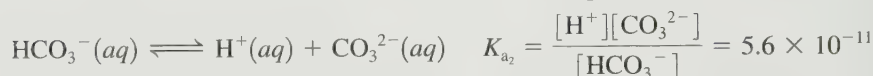
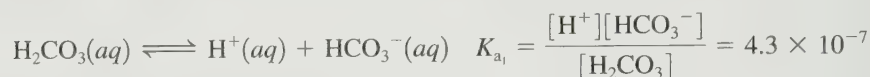
$$\text{pOH} = 1.68$$

$$\text{pH} = 14.00 - 1.68 = 12.32$$

See Exercises 14.85 and 14.86.

14.7 Polyprotic Acids

Some important acids, such as sulfuric acid (H_2SO_4) and phosphoric acid (H_3PO_4), can furnish more than one proton and are called **polyprotic acids**. A polyprotic acid always dissociates in a *stepwise* manner, one proton at a time. For example, the diprotic (two-proton) acid carbonic acid (H_2CO_3), which is so important in maintaining a constant pH in human blood, dissociates in the following steps:



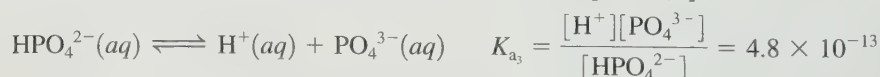
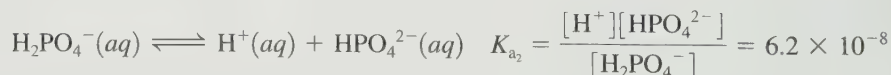
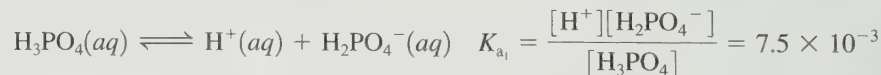
The successive K_a values for the dissociation equilibria are designated K_{a_1} and K_{a_2} . Note that the conjugate base HCO_3^- of the first dissociation equilibrium becomes the acid in the second step.

Carbonic acid is formed when carbon dioxide gas is dissolved in water. In fact, the first dissociation step for carbonic acid is best represented by the reaction



since relatively little H_2CO_3 actually exists in solution. However, it is convenient to consider CO_2 in water as H_2CO_3 so that we can treat such solutions using the familiar dissociation reactions for weak acids.

Phosphoric acid is a **triprotic acid** (three protons) that dissociates in the following steps:



For a typical weak polyprotic acid,

$$K_{a_1} > K_{a_2} > K_{a_3}$$

That is, the acid involved in each step of the dissociation is successively weaker, as shown by the stepwise dissociation constants given in Table 14.4. These values in-

TABLE 14.4 Stepwise Dissociation Constants for Several Common Polyprotic Acids

Name	Formula	K_{a1}	K_{a2}	K_{a3}
Phosphoric acid	H_3PO_4	7.5×10^{-3}	6.2×10^{-8}	4.8×10^{-13}
Arsenic acid	H_3AsO_4	5×10^{-3}	8×10^{-8}	6×10^{-10}
Carbonic acid	H_2CO_3	4.3×10^{-7}	5.6×10^{-11}	
Sulfuric acid	H_2SO_4	Large	1.2×10^{-2}	
Sulfurous acid	H_2SO_3	1.5×10^{-2}	1.0×10^{-7}	
Hydrosulfuric acid*	H_2S	1.0×10^{-7}	$\sim 10^{-19}$	
Oxalic acid	$\text{H}_2\text{C}_2\text{O}_4$	6.5×10^{-2}	6.1×10^{-5}	
Ascorbic acid (vitamin C)	$\text{H}_2\text{C}_6\text{H}_6\text{O}_6$	7.9×10^{-5}	1.6×10^{-12}	

*The K_{a2} value for H_2S is very uncertain. Because it is so small, the K_{a2} value is very difficult to measure accurately.

A table of K_a values for polyprotic acids is also given in Appendix 5.2.

dicates that the loss of a second or third proton occurs less readily than loss of the first proton. This is not surprising; as the negative charge on the acid increases, it becomes more difficult to remove the positively charged proton.

Although we might expect the pH calculations for solutions of polyprotic acids to be complicated, the most common cases are surprisingly straightforward. To illustrate, we will consider a typical case, phosphoric acid, and a unique case, sulfuric acid.

Phosphoric Acid

Phosphoric acid is typical of most polyprotic acids in that the successive K_a values are very different. For example, the ratios of successive K_a values (from Table 14.4) are

$$\begin{aligned}\frac{K_{a1}}{K_{a2}} &= \frac{7.5 \times 10^{-3}}{6.2 \times 10^{-8}} = 1.2 \times 10^5 \\ \frac{K_{a2}}{K_{a3}} &= \frac{6.2 \times 10^{-8}}{4.8 \times 10^{-13}} = 1.3 \times 10^5\end{aligned}$$

Thus the relative acid strengths are



For a typical polyprotic acid in water, only the first dissociation step is important in determining the pH.

This means that in a solution prepared by dissolving H_3PO_4 in water, *only the first dissociation step makes an important contribution to $[\text{H}^+]$* . This greatly simplifies the pH calculations for phosphoric acid solutions, as is illustrated in Sample Exercise 14.15.

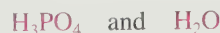
SAMPLE EXERCISE 14.15

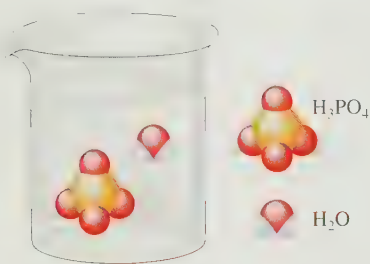
The pH of a Polyprotic Acid

Calculate the pH of a 5.0 M H_3PO_4 solution and the equilibrium concentrations of the species H_3PO_4 , H_2PO_4^- , HPO_4^{2-} , and PO_4^{3-} .

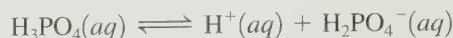
SOLUTION

The major species in solution are





None of the dissociation products of H_3PO_4 is written, since the K_a values are all so small that they will be minor species. The dominant equilibrium is the dissociation of H_3PO_4 :



where

$$K_{a_1} = 7.5 \times 10^{-3} = \frac{[\text{H}^+][\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]}$$

The ICE table is:

	$\text{H}_3\text{PO}_4(aq)$	$\rightleftharpoons$	$\text{H}^+(aq)$	+	$\text{H}_2\text{PO}_4^-(aq)$
Initial:	5.0		0		0
Change:	$-x$		$+x$		$+x$
Equilibrium:	$5.0 - x$		x		x

Substituting the equilibrium concentrations into the expression for K_{a_1} and making the usual approximation give

$$K_{a_1} = 7.5 \times 10^{-3} = \frac{[\text{H}^+][\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]} = \frac{(x)(x)}{5.0 - x} \approx \frac{x^2}{5.0}$$

Thus

$$x \approx 1.9 \times 10^{-1}$$

Since 1.9×10^{-1} is less than 5% of 5.0, the approximation is acceptable, and

$$[\text{H}^+] = x = 0.19 \text{ M}$$

$$\text{pH} = 0.72$$

So far we have determined that

$$[\text{H}^+] = [\text{H}_2\text{PO}_4^-] = 0.19 \text{ M}$$

and

$$[\text{H}_3\text{PO}_4] = 5.0 - x = 4.8 \text{ M}$$

The concentration of HPO_4^{2-} can be obtained by using the expression for K_{a_2} :

$$K_{a_2} = 6.2 \times 10^{-8} = \frac{[\text{H}^+][\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]}$$

where

$$[\text{H}^+] = [\text{H}_2\text{PO}_4^-] = 0.19 \text{ M}$$

Thus

$$[\text{HPO}_4^{2-}] = K_{a_2} = 6.2 \times 10^{-8} \text{ M}$$

To calculate $[\text{PO}_4^{3-}]$, we use the expression for K_{a_3} and the values of $[\text{H}^+]$ and $[\text{HPO}_4^{2-}]$ calculated previously:

$$K_{a_3} = \frac{[\text{H}^+][\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]} = 4.8 \times 10^{-13} = \frac{0.19[\text{PO}_4^{3-}]}{(6.2 \times 10^{-8})}$$

$$[\text{PO}_4^{3-}] = \frac{(4.8 \times 10^{-13})(6.2 \times 10^{-8})}{0.19} = 1.6 \times 10^{-19} \text{ M}$$

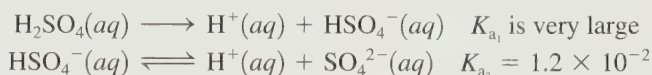
These results show that the second and third dissociation steps do not make an important contribution to $[\text{H}^+]$. This is apparent from the fact that $[\text{HPO}_4^{2-}]$ is $6.2 \times 10^{-8} \text{ M}$, which means that only $6.2 \times 10^{-8} \text{ mol/L}$ H_3PO_4 has dissociated. The value of $[\text{PO}_4^{3-}]$ shows that the dissociation of HPO_4^{2-} is even smaller. We

must, however, use the second and third dissociation steps to calculate $[\text{HPO}_4^{2-}]$ and $[\text{PO}_4^{3-}]$, since these steps are the only sources of these ions.

See Exercises 14.95 and 14.96.

Sulfuric Acid

Sulfuric acid is unique among the common acids in that it is a *strong acid in its first dissociation step and a weak acid in its second step*:



Sample Exercise 14.16 illustrates how to calculate the pH for sulfuric acid solutions.

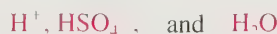
SAMPLE EXERCISE 14.16

The pH of Sulfuric Acid

Calculate the pH of a 1.0 M H_2SO_4 solution.

SOLUTION

The major species in the solution are



where the first two ions are produced by the complete first dissociation step of H_2SO_4 . The concentration of H^+ in this solution will be at least 1.0 M, since this amount is produced by the first dissociation step of H_2SO_4 . We must now answer this question: Does the HSO_4^- ion dissociate enough to produce a significant contribution to the concentration of H^+ ? This question can be answered by calculating the equilibrium concentrations for the dissociation reactions of HSO_4^- :



where

$$K_{a_2} = 1.2 \times 10^{-2} = \frac{[\text{H}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]}$$

The ICE table is:

	$\text{HSO}_4^-(\text{aq})$	$\rightleftharpoons$	$\text{H}^+(\text{aq})$	+	$\text{SO}_4^{2-}(\text{aq})$
Initial:	1.0		1.0		0
Change:	$-x$		$+x$		$+x$
Equilibrium:	$1.0 - x$		$1.0 + x$		x

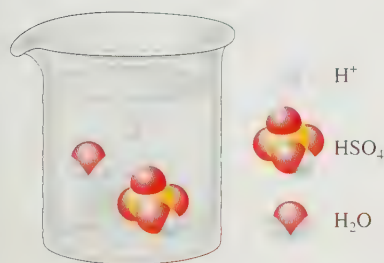
Note that $[\text{H}^+]_0$ is not equal to zero, as it usually is for a weak acid, because the first dissociation step has already occurred. Substituting the equilibrium concentrations into the expression for K_{a_2} and making the usual approximation give

$$K_{a_2} = 1.2 \times 10^{-2} = \frac{[\text{H}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]} = \frac{(1.0 + x)(x)}{1.0 - x} \approx \frac{(1.0)(x)}{(1.0)}$$

Thus

$$x \approx 1.2 \times 10^{-2}$$

Since 1.2×10^{-2} is 1.2% of 1.0, the approximation is valid according to the 5% rule. Note that x is not equal to $[\text{H}^+]$ in this case. Instead,



A bottle of sulfuric acid.

$$\begin{aligned}
 [\text{H}^+] &= 1.0\text{ M} + x = 1.0\text{ M} + (1.2 \times 10^{-2})\text{ M} \\
 &= 1.0\text{ M} \quad (\text{to the correct number of significant figures})
 \end{aligned}$$

Thus the dissociation of HSO_4^- does not make a significant contribution to the concentration of H^+ , and

$$[\text{H}^+] = 1.0\text{ M} \quad \text{and} \quad \text{pH} = 0.00$$

See Exercise 14.97.

Only in dilute H_2SO_4 solutions does the second dissociation step contribute significantly to $[\text{H}^+]$.

Sample Exercise 14.16 illustrates the most common case for sulfuric acid in which only the first dissociation makes an important contribution to the concentration of H^+ . In solutions more dilute than 1.0 M (for example, 0.10 M H_2SO_4), the dissociation of HSO_4^- is important, and solving the problem requires use of the quadratic formula, as shown in Sample Exercise 14.17.

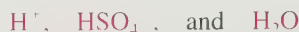
SAMPLE EXERCISE 14.17

The pH of Sulfuric Acid

Calculate the pH of a $1.00 \times 10^{-2}\text{ M}$ H_2SO_4 solution.

SOLUTION

The major species in solution are



Proceeding as in Sample Exercise 14.16, we consider the dissociation of HSO_4^- , which leads to the following ICE table:

	$\text{HSO}_4^-(aq)$	$\rightleftharpoons$	$\text{H}^+(aq)$	+	$\text{SO}_4^{2-}(aq)$
Initial:	0.0100		0.0100		0
			From dissociation of H_2SO_4		
Change:	$-x$		$+x$		$+x$
Equilibrium:	$0.0100 - x$		$0.0100 + x$		x

Substituting the equilibrium concentrations into the expression for K_{a_2} gives

$$1.2 \times 10^{-2} = K_{a_2} = \frac{[\text{H}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]} = \frac{(0.0100 + x)(x)}{(0.0100 - x)}$$

If we make the usual approximation, then $0.0100 + x \approx 0.0100$ and $0.0100 - x \approx 0.0100$, and we have

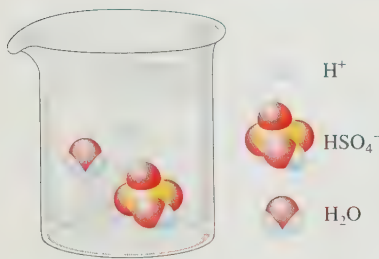
$$1.2 \times 10^{-2} = \frac{(0.0100 + x)(x)}{(0.0100 - x)} \approx \frac{(0.0100)x}{(0.0100)}$$

The calculated value of x is

$$x = 1.2 \times 10^{-2} = 0.012$$

This value is larger than 0.010, clearly a ridiculous result. Thus we cannot make the usual approximation and must instead solve the quadratic equation. The expression

$$1.2 \times 10^{-2} = \frac{(0.0100 + x)(x)}{(0.0100 - x)}$$



$$\begin{aligned} \text{leads to} \quad & (1.2 \times 10^{-2})(0.0100 - x) = (0.0100 + x)(x) \\ & (1.2 \times 10^{-4}) - (1.2 \times 10^{-2})x = (1.0 \times 10^{-2})x + x^2 \\ & x^2 + (2.2 \times 10^{-2})x - (1.2 \times 10^{-4}) = 0 \end{aligned}$$

This equation can be solved using the quadratic formula

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

where $a = 1$, $b = 2.2 \times 10^{-2}$, and $c = -1.2 \times 10^{-4}$. Use of the quadratic formula gives one negative root (which cannot be correct) and one positive root,

$$x = 4.5 \times 10^{-3}$$

$$\text{Thus} \quad [\text{H}^+] = 0.0100 + x = 0.0100 + 0.0045 = 0.0145$$

$$\text{and} \quad \text{pH} = 1.84$$

Note that in this case the second dissociation step produces about half as many H^+ ions as the initial step does.

This problem also can be solved by successive approximations, a method illustrated in Appendix 1.4.

See Exercise 14.98.

Characteristics of Weak Polyprotic Acids

1. Typically, successive K_a values are so much smaller than the first value that only the first dissociation step makes a significant contribution to the equilibrium concentration of H^+ . This means that the calculation of the pH for a solution of a typical weak polyprotic acid is identical to that for a solution of a weak monoprotic acid.
2. Sulfuric acid is unique in being a strong acid in its first dissociation step and a weak acid in its second step. For relatively concentrated solutions of sulfuric acid (1.0 M or higher), the large concentration of H^+ from the first dissociation step represses the second step, which can be neglected as a contributor of H^+ ions. For dilute solutions of sulfuric acid, the second step does make a significant contribution, and the quadratic equation must be used to obtain the total H^+ concentration.

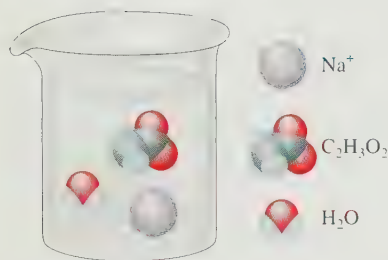
14.8 Acid-Base Properties of Salts

Salt is simply another name for *ionic compound*. When a salt dissolves in water, we assume that it breaks up into its ions, which move about independently, at least in dilute solutions. Under certain conditions, these ions can behave as acids or bases. In this section we explore such reactions.

Salts That Produce Neutral Solutions

Recall that the conjugate base of a strong acid has virtually no affinity for protons in water. This is why strong acids completely dissociate in aqueous solution. Thus, when anions such as Cl^- and NO_3^- are placed in water, they do not combine with H^+ and have no effect on the pH. Cations such as K^+ and Na^+ from strong bases

The salt of a strong acid and a strong base gives a neutral solution.



have no affinity for H^+ , nor can they produce H^+ , so they too have no effect on the pH of an aqueous solution. *Salts that consist of the cations of strong bases and the anions of strong acids have no effect on $[H^+]$ when dissolved in water.* This means that aqueous solutions of salts such as KCl, NaCl, $NaNO_3$, and KNO_3 are neutral (have a pH of 7).

Salts That Produce Basic Solutions

In an aqueous solution of sodium acetate ($NaC_2H_3O_2$), the major species are



What are the acid–base properties of each component? The Na^+ ion has neither acid nor base properties. The $C_2H_3O_2^-$ ion is the conjugate base of acetic acid, a weak acid. This means that $C_2H_3O_2^-$ has a significant affinity for a proton and is a base. Finally, water is a weakly amphoteric substance.

The pH of this solution will be determined by the $C_2H_3O_2^-$ ion. Since $C_2H_3O_2^-$ is a base, it will react with the best proton donor available. In this case, water is the only source of protons, and the reaction between the acetate ion and water is



Note that this reaction, which yields a base solution, involves a *base reacting with water to produce hydroxide ion and a conjugate acid*. We have defined K_b as the equilibrium constant for such a reaction. In this case,

$$K_b = \frac{[HC_2H_3O_2][OH^-]}{[C_2H_3O_2^-]}$$

The value of K_a for acetic acid is well known (1.8×10^{-5}). But how can we obtain the K_b value for the acetate ion? The answer lies in the relationships among K_a , K_b , and K_w . Note that when the expression for K_a for acetic acid is multiplied by the expression for K_b for the acetate ion, the result is K_w :

$$K_a \times K_b = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} \times \frac{[HC_2H_3O_2][OH^-]}{[C_2H_3O_2^-]} = [H^+][OH^-] = K_w$$

This is a very important result. For any weak acid and its conjugate base,

$$K_a \times K_b = K_w$$

Thus, when either K_a or K_b is known, the other can be calculated. For the acetate ion,

$$K_b = \frac{K_w}{K_a \text{ (for } HC_2H_3O_2)} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

This is the K_b value for the reaction described by Equation (14.7). Note that it is obtained from the K_a value of the parent weak acid, in this case acetic acid. The sodium acetate solution is an example of an important general case. *For any salt whose cation has neutral properties (such as Na^+ or K^+) and whose anion is the conjugate base of a weak acid, the aqueous solution will be basic.* The K_b value for the anion can be obtained from the relationship $K_b = K_w/K_a$. Equilibrium calculations of this type are illustrated in Sample Exercise 14.18.

A basic solution is formed if the anion of the salt is the conjugate base of a weak acid.

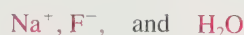
SAMPLE EXERCISE 14.18

Salts as Weak Bases

Calculate the pH of a 0.30 M NaF solution. The K_a value for HF is 7.2×10^{-4} .

SOLUTION

The major species in solution are



Since HF is a weak acid, the F^- ion must have a significant affinity for protons, and the dominant reaction will be



which yields the K_b expression

$$K_b = \frac{[\text{HF}][\text{OH}^-]}{[\text{F}^-]}$$

The value of K_b can be calculated from K_w and the K_a value for HF:

$$K_b = \frac{K_w}{K_a(\text{for HF})} = \frac{1.0 \times 10^{-14}}{7.2 \times 10^{-4}} = 1.4 \times 10^{-11}$$

The corresponding ICE table is:

	$\text{F}^-(aq)$	+	$\text{H}_2\text{O}(l)$	$\rightleftharpoons$	$\text{HF}(aq)$	+	$\text{OH}^-(aq)$
Initial:	0.30		—		0		≈ 0
Change:	$-x$		—		$+x$		$+x$
Equilibrium:	$0.30 - x$		—		x		x

$$\text{Thus } K_b = 1.4 \times 10^{-11} = \frac{[\text{HF}][\text{OH}^-]}{[\text{F}^-]} = \frac{(x)(x)}{0.30 - x} \approx \frac{x^2}{0.30}$$

and

$$x \approx 2.0 \times 10^{-6}$$

The approximation is valid by the 5% rule, so

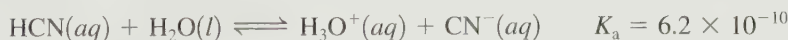
$$\begin{aligned} [\text{OH}^-] &= x = 2.0 \times 10^{-6} M \\ \text{pOH} &= 5.69 \\ \text{pH} &= 14.00 - 5.69 = 8.31 \end{aligned}$$

As expected, the solution is basic.

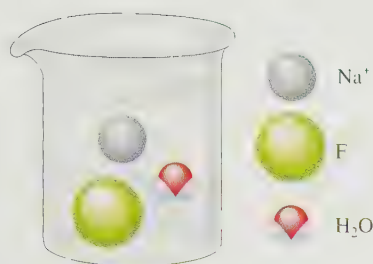
See Exercise 14.103.

Base Strength in Aqueous Solutions

To emphasize the concept of base strength, let us consider the basic properties of the cyanide ion. One relevant reaction is the dissociation of hydrocyanic acid in water:



Since HCN is such a weak acid, CN^- appears to be a *strong* base, showing a very high affinity for H^+ compared to H_2O , with which it is competing. However, we also need to look at the reaction in which cyanide ion reacts with water:





where

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{6.2 \times 10^{-10}} = 1.6 \times 10^{-5}$$

In this reaction CN^- appears to be a weak base; the K_b value is only 1.6×10^{-5} . What accounts for this apparent difference in base strength? The key idea is that in the reaction of CN^- with H_2O , CN^- is competing with OH^- for H^+ , instead of competing with H_2O , as it does in the HCN dissociation reaction. These equilibria show the following relative base strengths:



Similar arguments can be made for other “weak” bases, such as ammonia, the acetate ion, the fluoride ion, and so on.

Salts That Produce Acidic Solutions

Some salts produce acidic solutions when dissolved in water. For example, when solid NH_4Cl is dissolved in water, NH_4^+ and Cl^- ions are present, with NH_4^+ behaving as a weak acid:



The Cl^- ion, having virtually no affinity for H^+ in water, does not affect the pH of the solution.

In general, *salts in which the anion is not a base and the cation is the conjugate acid of a weak base produce acidic solutions.*

SAMPLE EXERCISE 14.19

Salts as Weak Acids I

Calculate the pH of a 0.10 M NH_4Cl solution. The K_b value for NH_3 is 1.8×10^{-5} .

SOLUTION

The major species in solution are



Note that both NH_4^+ and H_2O can produce H^+ . The dissociation reaction for the NH_4^+ ion is



for which

$$K_a = \frac{[\text{NH}_3][\text{H}^+]}{[\text{NH}_4^+]}$$

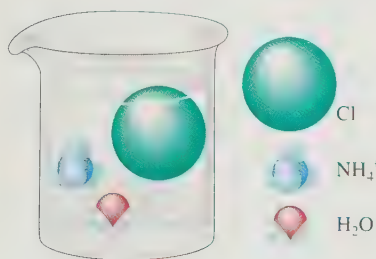
Note that although the K_b value for NH_3 is given, the reaction corresponding to K_b is not appropriate here, since NH_3 is not a major species in the solution. Instead, the given value of K_b is used to calculate K_a for NH_4^+ from the relationship

$$K_a \times K_b = K_w$$

Thus

$$K_a (\text{for } \text{NH}_4^+) = \frac{K_w}{K_b (\text{for } \text{NH}_3)} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

Although NH_4^+ is a very weak acid, as indicated by its K_a value, it is stronger than H_2O and will dominate in the production of H^+ . Thus we will focus on the dissociation reaction of NH_4^+ to calculate the pH in this solution.



We solve the weak acid problem in the usual way:

	$\text{NH}_4^+(aq)$	$\rightleftharpoons$	$\text{H}^+(aq)$	+	$\text{NH}_3(aq)$
Initial:	0.10		≈ 0		0
Change:	$-x$		$+x$		$+x$
Equilibrium:	$0.10 - x$		x		x

Thus

$$5.6 \times 10^{-10} = K_a = \frac{[\text{H}^+][\text{NH}_3]}{[\text{NH}_4^+]} = \frac{(x)(x)}{0.10 - x} \approx \frac{x^2}{0.10}$$

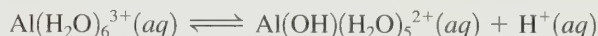
$$x \approx 7.5 \times 10^{-6}$$

The approximation is valid by the 5% rule, so

$$[\text{H}^+] = x = 7.5 \times 10^{-6} M \quad \text{and} \quad \text{pH} = 5.13$$

See Exercise 14.104.

A second type of salt that produces an acidic solution is one that contains a *highly charged metal ion*. For example, when solid aluminum chloride (AlCl_3) is dissolved in water, the resulting solution is significantly acidic. Although the Al^{3+} ion is not itself a Brønsted–Lowry acid, the hydrated ion $\text{Al}(\text{H}_2\text{O})_6^{3+}$ formed in water is a weak acid:



The high charge on the metal ion polarizes the O—H bonds in the attached water molecules, making the hydrogens in these water molecules more acidic than those in free water molecules. Typically, the higher the charge on the metal ion, the stronger the acidity of the hydrated ion.

Section 14.9 contains a further discussion of the acidity of hydrated ions.

SAMPLE EXERCISE 14.20

Salts as Weak Acids II

Calculate the pH of a 0.010 M AlCl_3 solution. The K_a value for $\text{Al}(\text{H}_2\text{O})_6^{3+}$ is 1.4×10^{-5} .

SOLUTION

The major species in solution are



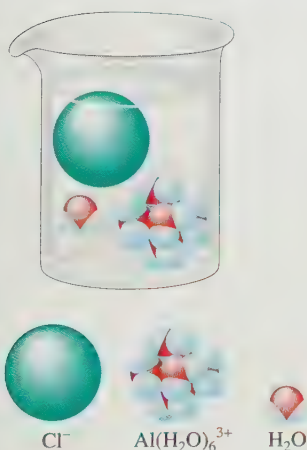
Since the $\text{Al}(\text{H}_2\text{O})_6^{3+}$ ion is a stronger acid than water, the dominant equilibrium is



$$\text{and} \quad 1.4 \times 10^{-5} = K_a = \frac{[\text{Al}(\text{OH})(\text{H}_2\text{O})_5^{2+}][\text{H}^+]}{[\text{Al}(\text{H}_2\text{O})_6^{3+}]}$$

This is a typical weak acid problem, which we can solve with the usual procedure:

	$\text{Al}(\text{H}_2\text{O})_6^{3+}(aq)$	$\rightleftharpoons$	$\text{Al}(\text{OH})(\text{H}_2\text{O})_5^{2+}(aq)$	+	$\text{H}^+(aq)$
Initial:	0.010		0		≈ 0
Change:	$-x$		$+x$		$+x$
Equilibrium:	$0.010 - x$		x		x



Thus

$$1.4 \times 10^{-5} = K_a = \frac{[\text{Al}(\text{OH})(\text{H}_2\text{O})_5^{2+}][\text{H}^+]}{[\text{Al}(\text{H}_2\text{O})_6^{3+}]} = \frac{(x)(x)}{0.010 - x} \approx \frac{x^2}{0.010}$$

$$x \approx 3.7 \times 10^{-4}$$

Since the approximation is valid by the 5% rule,

$$[\text{H}^+] = x = 3.7 \times 10^{-4} M \quad \text{and} \quad \text{pH} = 3.43$$

See Exercises 14.109 and 14.110.

TABLE 14.5

Qualitative Prediction of pH for Solutions of Salts for Which Both Cation and Anion Have Acidic or Basic Properties

$K_a > K_b$	pH < 7 (acidic)
$K_b > K_a$	pH > 7 (basic)
$K_a = K_b$	pH = 7 (neutral)

So far we have considered salts in which only one of the ions has acidic or basic properties. For many salts, such as ammonium acetate ($\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$), both ions can affect the pH of the aqueous solution. Because the equilibrium calculations for these cases can be quite complicated, we will consider only the qualitative aspects of such problems. We can predict whether the solution will be basic, acidic, or neutral by comparing the K_a value for the acidic ion with the K_b value for the basic ion. If the K_a value for the acidic ion is larger than the K_b value for the basic ion, the solution will be acidic. If the K_b value is larger than the K_a value, the solution will be basic. Equal K_a and K_b values mean a neutral solution. These facts are summarized in Table 14.5.

SAMPLE EXERCISE 14.21

The Acid–Base Properties of Salts

Predict whether an aqueous solution of each of the following salts will be acidic, basic, or neutral.

- a. $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ b. NH_4CN c. $\text{Al}_2(\text{SO}_4)_3$

SOLUTION

- a. The ions in solution are NH_4^+ and $\text{C}_2\text{H}_3\text{O}_2^-$. As we mentioned previously, K_a for NH_4^+ is 5.6×10^{-10} and K_b for $\text{C}_2\text{H}_3\text{O}_2^-$ is 5.6×10^{-10} . Thus K_a for NH_4^+ is equal to K_b for $\text{C}_2\text{H}_3\text{O}_2^-$, and the solution will be neutral (pH = 7).
- b. The solution will contain NH_4^+ and CN^- ions. The K_a value for NH_4^+ is 5.6×10^{-10} and

$$K_b(\text{for } \text{CN}^-) = \frac{K_w}{K_a(\text{for } \text{HCN})} = 1.6 \times 10^{-5}$$

Since K_b for CN^- is much larger than K_a for NH_4^+ , CN^- is a much stronger base than NH_4^+ is an acid. This solution will be basic.

- c. The solution will contain $\text{Al}(\text{H}_2\text{O})_6^{3+}$ and SO_4^{2-} ions. The K_a value for $\text{Al}(\text{H}_2\text{O})_6^{3+}$ is 1.4×10^{-5} , as given in Sample Exercise 14.20. We must calculate K_b for SO_4^{2-} . The HSO_4^- ion is the conjugate acid of SO_4^{2-} , and its K_a value is K_{a2} for sulfuric acid, or 1.2×10^{-2} . Therefore,

$$K_b(\text{for } \text{SO}_4^{2-}) = \frac{K_w}{K_{a2}(\text{for sulfuric acid})}$$

$$= \frac{1.0 \times 10^{-14}}{1.2 \times 10^{-2}} = 8.3 \times 10^{-13}$$

This solution will be acidic, since K_a for $\text{Al}(\text{H}_2\text{O})_6^{3+}$ is much greater than K_b for SO_4^{2-} .

See Exercises 14.111 and 14.112.

TABLE 14.6 Acid–Base Properties of Various Types of Salts

Type of Salt	Examples	Comment	pH of Solution
Cation is from strong base; anion is from strong acid	KCl, KNO ₃ , NaCl, NaNO ₃	Neither acts as an acid or a base	Neutral
Cation is from strong base; anion is from weak acid	NaC ₂ H ₃ O ₂ , KCN, NaF	Anion acts as a base; cation has no effect on pH	Basic
Cation is conjugate acid of weak base; anion is from strong acid	NH ₄ Cl, NH ₄ NO ₃	Cation acts as acid; anion has no effect on pH	Acidic
Cation is conjugate acid of weak base; anion is conjugate base of weak acid	NH ₄ C ₂ H ₃ O ₂ , NH ₄ CN	Cation acts as an acid; anion acts as a base	Acidic if $K_a > K_b$, basic if $K_b > K_a$, neutral if $K_a = K_b$
Cation is highly charged metal ion; anion is from strong acid	Al(NO ₃) ₃ , FeCl ₃	Hydrated cation acts as an acid; anion has no effect on pH	Acidic

The acid–base properties of aqueous solutions of various salts are summarized in Table 14.6.

14.9 The Effect of Structure on Acid–Base Properties

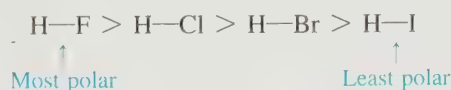
Further aspects of acid strengths are discussed in Section 20.7.

We have seen that when a substance is dissolved in water, it produces an acidic solution if it can donate protons and produces a basic solution if it can accept protons. What structural properties of a molecule cause it to behave as an acid or as a base?

Any molecule containing a hydrogen atom is potentially an acid. However, many such molecules show no acidic properties. For example, molecules containing C—H bonds, such as chloroform (CHCl₃) and nitromethane (CH₃NO₂), do not produce acidic aqueous solutions because a C—H bond is both strong and nonpolar and thus there is no tendency to donate protons. On the other hand, although the H—Cl bond in gaseous hydrogen chloride is slightly stronger than a C—H bond, it is much more polar, and this molecule readily dissociates when dissolved in water.

Thus there are two main factors that determine whether a molecule containing an X—H bond will behave as a Brønsted–Lowry acid: the strength of the bond and the polarity of the bond.

To explore these factors let's consider the relative acid strengths of the hydrogen halides. The bond polarities vary as shown

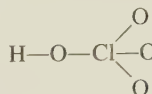
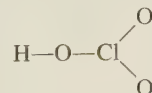
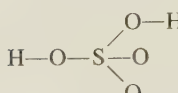
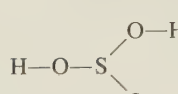
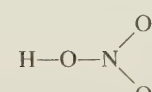


because electronegativity decreases going down the group. Based on the high polarity of the H—F bond, we might expect hydrogen fluoride to be a very strong acid. In fact, among HX molecules, HF is the only weak acid ($K_a = 7.2 \times 10^{-4}$) when dissolved in water. The H—F bond is unusually strong, as shown in Table 14.7, and thus is difficult to break. This contributes significantly to the reluctance of the HF molecules to dissociate in water.

TABLE 14.7 Bond Strengths and Acid Strengths for Hydrogen Halides

H—X Bond	Bond Strength (kJ/mol)	Acid Strength in Water
H—F	565	Weak
H—Cl	427	Strong
H—Br	363	Strong
H—I	295	Strong

TABLE 14.8 Several Series of Oxyacids and Their K_a Values

Oxyacid	Structure	K_a Value
HClO_4		Large ($\sim 10^7$)
HClO_3		~ 1
HClO_2	$\text{H}-\text{O}-\text{Cl}-\text{O}$	1.2×10^{-2}
HClO	$\text{H}-\text{O}-\text{Cl}$	3.5×10^{-8}
H_2SO_4		Large
H_2SO_3		1.5×10^{-2}
HNO_3		Large
HNO_2	$\text{H}-\text{O}-\text{N}-\text{O}$	4.0×10^{-4}

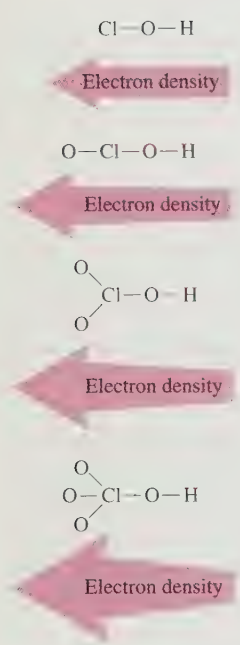


FIGURE 14.11
The effect of the number of attached oxygens on the O—H bond in a series of chlorine oxyacids. As the number of oxygen atoms attached to the chlorine atom increases, they become more effective at withdrawing electron density from the O—H bond, thereby weakening and polarizing it. This increases the tendency for the molecule to produce a proton, and so its acid strength increases.

Another important class of acids are the oxyacids, which as we saw in Section 14.2 characteristically contain the grouping H—O—X. Several series of oxyacids are listed with their K_a values in Table 14.8. Note from these data that for a given series the acid strength increases with an increase in the number of oxygen atoms attached to the central atom. For example, in the series containing chlorine and a varying number of oxygen atoms, HOCl is a weak acid, but the acid strength is successively greater as the number of oxygen atoms increases. This happens because the very electronegative oxygen atoms are able to draw electrons away from the chlorine atom and the O—H bond, as shown in Fig. 14.11. The net effect is to both polarize and weaken the O—H bond; this effect is more important as the number of attached oxygen atoms increases. This means that a proton is most readily produced by the molecule with the largest number of attached oxygen atoms (HClO_4).

This type of behavior is also observed for hydrated metal ions. Earlier in this chapter we saw that highly charged metal ions such as Al^{3+} produce acidic solutions. The acidity of the water molecules attached to the metal ion is increased by the attraction of electrons to the positive metal ion:

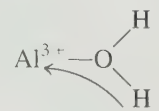


TABLE 14.9 Comparison of Electronegativity of X and K_a Value for a Series of Oxyacids

Acid	X	Electronegativity of X	K_a for Acid
HOCl	Cl	3.0	4×10^{-8}
HOBr	Br	2.8	2×10^{-9}
HOI	I	2.5	2×10^{-11}
HOCH ₃	CH ₃	2.3 (for carbon in CH ₃)	$\sim 10^{-15}$

The greater the charge on the metal ion, the more acidic the hydrated ion becomes.

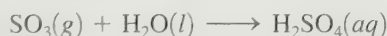
For acids containing the H—O—X grouping, the greater the ability of X to draw electrons toward itself, the greater the acidity of the molecule. Since the electronegativity of X reflects its ability to attract the electrons involved in bonding, we might expect acid strength to depend on the electronegativity of X. In fact, there is an excellent correlation between the electronegativity of X and the acid strength for oxyacids, as shown in Table 14.9.

14.10 Acid-Base Properties of Oxides

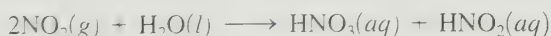
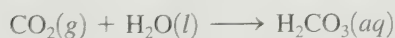
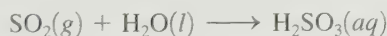
A compound containing the H—O—X group will produce an acidic solution in water if the O—X bond is strong and covalent. If the O—X bond is ionic, the compound will produce a basic solution in water.

We have just seen that molecules containing the grouping H—O—X can behave as acids and that the acid strength depends on the electron-withdrawing ability of X. But substances with this grouping also can behave as bases if the hydroxide ion instead of a proton is produced. What determines which behavior will occur? The answer lies mainly in the nature of the O—X bond. If X has a relatively high electronegativity, the O—X bond will be covalent and strong. When the compound containing the H—O—X grouping is dissolved in water, the O—X bond will remain intact. It will be the polar and relatively weak H—O bond that will tend to break, releasing a proton. On the other hand, if X has a very low electronegativity, the O—X bond will be ionic and subject to being broken in polar water. Examples are the ionic substances NaOH and KOH that dissolve in water to give the metal cation and the hydroxide ion.

We can use these principles to explain the acid-base behavior of oxides when they are dissolved in water. For example, when a covalent oxide such as sulfur trioxide is dissolved in water, an acidic solution results because sulfuric acid is formed:



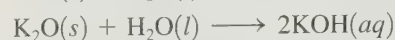
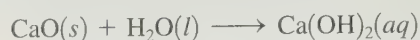
The structure of H₂SO₄ is shown in the margin. In this case, the strong, covalent O—S bonds remain intact and the H—O bonds break to produce protons. Other common covalent oxides that react with water to form acidic solutions are sulfur dioxide, carbon dioxide, and nitrogen dioxide, as shown by the following reactions:



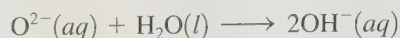
Thus, when a covalent oxide dissolves in water, an acidic solution forms. These oxides are called **acidic oxides**.



On the other hand, when an ionic oxide dissolves in water, a basic solution results, as shown by the following reactions:



These reactions can be explained by recognizing that the oxide ion has a high affinity for protons and reacts with water to produce hydroxide ions:

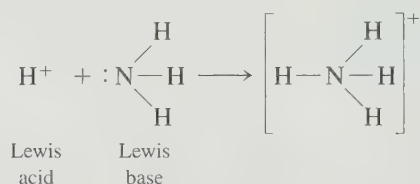


Thus the most ionic oxides, such as those of the Group 1A and 2A metals, produce basic solutions when they are dissolved in water. As a result, these oxides are called **basic oxides**.

14.11 The Lewis Acid–Base Model

We have seen that the first successful conceptualization of acid–base behavior was proposed by Arrhenius. This useful but limited model was replaced by the more general Brønsted–Lowry model. An even more general model for acid–base behavior was suggested by G. N. Lewis in the early 1920s. A **Lewis acid** is an *electron-pair acceptor*, and a **Lewis base** is an *electron-pair donor*. Another way of saying this is that a Lewis acid has an empty atomic orbital that it can use to accept (share) an electron pair from a molecule that has a lone pair of electrons (Lewis base). The three models for acids and bases are summarized in Table 14.10.

Note that Brønsted–Lowry acid–base reactions (proton donor–proton acceptor reactions) are encompassed by the Lewis model. For example, the reaction between a proton and an ammonia molecule, that is,



can be represented as a reaction between an electron-pair acceptor (H^+) and an electron-pair donor (NH_3). The same holds true for a reaction between a proton and a hydroxide ion:

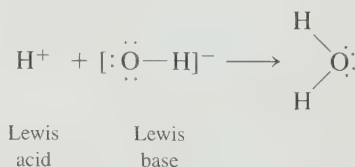


TABLE 14.10 Three Models for Acids and Bases

Model	Definition of Acid	Definition of Base
Arrhenius	H^+ producer	OH^- producer
Brønsted–Lowry	H^+ donor	H^+ acceptor
Lewis	Electron-pair acceptor	Electron-pair donor

CHEMICAL IMPACT

Self-Destructing Paper

The New York City Public Library has 88 miles of bookshelves, and on 36 miles of these shelves the books are quietly disintegrating between their covers. In fact, an estimated 40% of the books in the major research collections in the United States will soon be too fragile to handle.

The problem results from the acidic paper widely used in printing books in the past century. Ironically, books from the eighteenth, seventeenth, sixteenth, and even fifteenth century are in much better shape. Gutenberg Bibles contain paper that is in remarkably good condition. In those days, paper was made by hand from linen or rags, but in the nineteenth century, the demand for cheap paper skyrocketed.

Paper manufacturers found that paper could be made economically, by machine, using wood pulp. To size the paper (that is, fill in microscopic holes to lower absorption of moisture and prevent seeping or spreading of inks), alum [$\text{Al}_2(\text{SO}_4)_3$] was added in large amounts. Because the hydrated aluminum ion [$\text{Al}(\text{H}_2\text{O})_6^{3+}$] is an acid ($K_a \approx 10^{-5}$), paper manufactured using alum is quite acidic. Over time this acidity causes the paper fibers to disintegrate; the pages of books fall apart when they are used.

One could transfer the contents of the threatened books to microfilm, but that would be a very slow and expensive process. Can the books be chemically treated to neutralize the acid and stop the deterioration? Yes. In fact, you know enough chemistry at this point to design the treatment patented in 1936 by Otto Schierholz. He dipped individual pages in solutions of alkaline earth bicarbonate salts [$\text{Mg}(\text{HCO}_3)_2$, $\text{Ca}(\text{HCO}_3)_2$, and so on]. The HCO_3^- ions present in these solutions react with the H^+ in the paper to give CO_2 and H_2O . This treatment works well and is used today to preserve especially important works, but it is slow and labor-intensive.

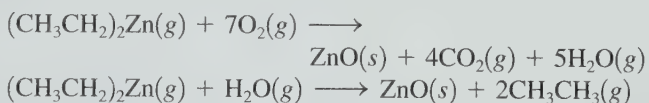
It would be much more economical if large numbers of books could be treated at one time without disturbing the bindings. However, soaking entire books in an aqueous solution is out of the question. A logical question then is: Are there gaseous bases that could be used to neutralize the acid? Certainly; the organic amines (general formula, RNH_2) are bases, and those with low molar masses are gases under normal conditions. Experiments in which books were treated using ammonia, butylamine ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$), and



A book ravaged by the decomposition of acidic paper.

other amines have shown that the method works, but only for a short time. The amines do enter the paper and neutralize the acid, but being volatile, they gradually evaporate, leaving the paper in its original acidic condition.

A much more effective treatment involves diethylzinc [$(\text{CH}_3\text{CH}_2)_2\text{Zn}$], which boils at 117°C and 1 atm. Diethylzinc (DEZ) reacts with oxygen or water to produce ZnO as follows:



The solid zinc oxide produced in these reactions is deposited among the paper fibers, and being a basic oxide, it neutralizes the acid present as shown in the equation



One major problem is that DEZ ignites spontaneously on contact with air. Therefore, this treatment must be carried out in a chamber filled mainly with $\text{N}_2(\text{g})$, where the amount of O_2 present can be rigorously controlled. The pressure in the chamber must be maintained well below one atmosphere both to lower the boiling point of DEZ and to remove excess moisture from the book's pages. Several major DEZ fires have slowed its implementation as a book preservative. However, the Library of Congress has designed a new DEZ treatment plant that includes a chamber large enough for approximately 9000 books to be treated at one time.

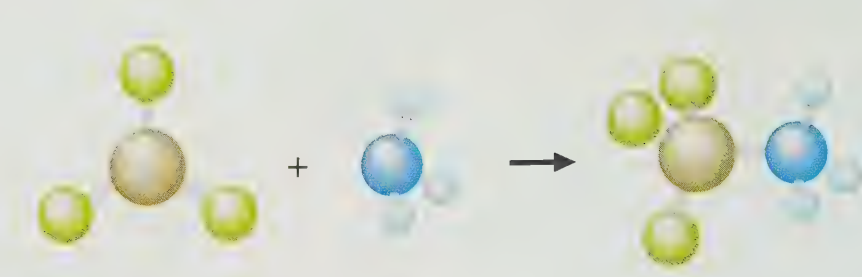
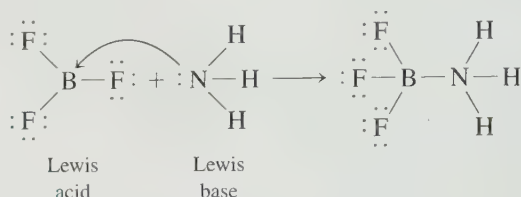


FIGURE 14.12
Reaction of BF_3 with NH_3 .

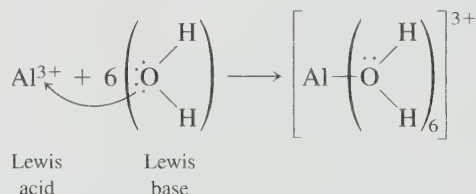
The Lewis model encompasses the Brønsted–Lowry model, but the reverse is not true.

The real value of the Lewis model for acids and bases is that it covers many reactions that do not involve Brønsted–Lowry acids. For example, consider the gas-phase reaction between boron trifluoride and ammonia.



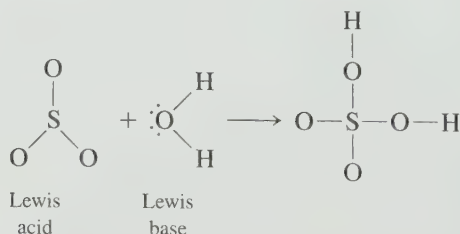
Here the electron-deficient BF_3 molecule (there are only six electrons around the boron) completes its octet by reacting with NH_3 , which has a lone pair of electrons. (see Fig. 14.12.) In fact, as mentioned in Chapter 8, the electron deficiency of boron trifluoride makes it very reactive toward any electron-pair donor. That is, it is a strong Lewis acid.

The hydration of a metal ion, such as Al^{3+} , also can be viewed as a Lewis acid–base reaction:



Here the Al^{3+} ion accepts one electron pair from each of six water molecules to form $\text{Al}(\text{H}_2\text{O})_6^{3+}$ (see Fig. 14.13).

In addition, the reaction between a covalent oxide and water to form a Brønsted–Lowry acid can be defined as a Lewis acid–base reaction. An example is the reaction between sulfur trioxide and water:



Note that as the water molecule attaches to sulfur trioxide, a proton shift occurs to form sulfuric acid.

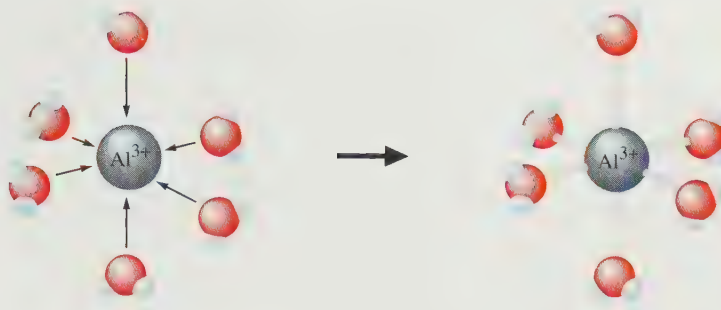


FIGURE 14.13
The $\text{Al}(\text{H}_2\text{O})_6^{3+}$ ion.

SAMPLE EXERCISE 14.22

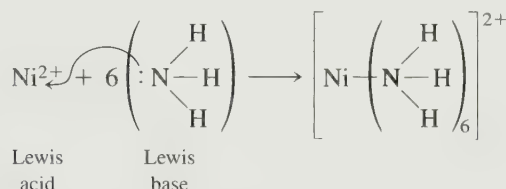
Lewis Acids and Bases

For each reaction, identify the Lewis acid and base.

- $\text{Ni}^{2+}(\text{aq}) + 6\text{NH}_3(\text{aq}) \longrightarrow \text{Ni}(\text{NH}_3)_6^{2+}(\text{aq})$
- $\text{H}^+(\text{aq}) + \text{H}_2\text{O}(\text{aq}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq})$

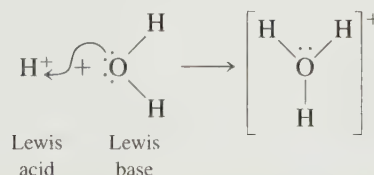
SOLUTION

- Each NH_3 molecule donates an electron pair to the Ni^{2+} ion:



The nickel(II) ion is the Lewis acid, and ammonia is the Lewis base.

- The proton is the Lewis acid and the water molecule is the Lewis base:



See Exercises 14.119 and 14.120.

14.12 Strategy for Solving Acid–Base Problems: A Summary

In this chapter we have encountered many different situations involving aqueous solutions of acids and bases, and in the next chapter we will encounter still more. In solving for the equilibrium concentrations in these aqueous solutions, it is tempting to create a pigeonhole for each possible situation and to memorize the procedures necessary to deal with that particular case. This approach is just not practical and

usually leads to frustration: Too many pigeonholes are required—there seems to be an infinite number of cases. But you can handle any case successfully by taking a systematic, patient, and thoughtful approach. When analyzing an acid–base equilibrium problem, do *not* ask yourself how a memorized solution can be used to solve the problem. Instead, ask this question: *What are the major species in the solution and what is their chemical behavior?*

The most important part of doing a complicated acid–base equilibrium problem is the analysis you do at the beginning of a problem.

What major species are present?

Does a reaction occur that can be assumed to go to completion?

What equilibrium dominates the solution?

Let the problem guide you. Be patient.

The following steps outline a general strategy for solving problems involving acid–base equilibria.

Solving Acid–Base Problems

- ➡ **1** List the major species in solution.
- ➡ **2** Look for reactions that can be assumed to go to completion—for example, a strong acid dissociating or H^+ reacting with OH^- .
- ➡ **3** For a reaction that can be assumed to go to completion:
 - a. Determine the concentration of the products.
 - b. Write down the major species in solution after the reaction.
- ➡ **4** Look at each major component of the solution and decide if it is an acid or a base.
- ➡ **5** Pick the equilibrium that will control the pH. Use known values of the dissociation constants for the various species to help decide on the dominant equilibrium.
 - a. Write the equation for the reaction and the equilibrium expression.
 - b. Compute the initial concentrations (assuming the dominant equilibrium has not yet occurred, that is, no acid dissociation, and so on).
 - c. Define x .
 - d. Compute the equilibrium concentrations in terms of x .
 - e. Substitute the concentrations into the equilibrium expression, and solve for x .
 - f. Check the validity of the approximation.
 - g. Calculate the pH and other concentrations as required.

Although these steps may seem somewhat cumbersome, especially for simpler problems, they will become increasingly helpful as the aqueous solutions become more complicated. If you develop the habit of approaching acid–base problems systematically, the more complex cases will be much easier to manage.

Key Terms

Section 14.1

Arrhenius concept
Brønsted–Lowry model
hydronium ion
conjugate base
conjugate acid
conjugate acid–base pair
acid dissociation constant

Section 14.2

strong acid
weak acid
diprotic acid
oxyacids
organic acids
carboxyl group
monoprotic acids
amphoteric substance
autoionization
ion-product (dissociation)
constant

Section 14.3

pH scale

Section 14.4

major species

Section 14.5

percent dissociation

Section 14.6

strong bases
slaked lime
lime–soda process
amine
weak base

Section 14.7

polyprotic acid
triprotic acid

Section 14.8

salt

Section 14.10

acidic oxide
basic oxide

Section 14.11

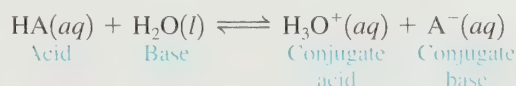
Lewis acid
Lewis base

For Review

Summary

In this chapter we have developed several models of acid–base behavior and have applied fundamental equilibrium principles to calculate the pH values for solutions of acids and bases.

Arrhenius postulated that acids produce H^+ ions in solutions and bases produce OH^- ions. The Brønsted–Lowry model is more general: An acid is a proton donor, and a base is a proton acceptor. Water acts as a Brønsted–Lowry base when it accepts a proton from an acid to form a hydronium ion:



A conjugate base is everything that remains of the acid molecule after the proton is lost. A conjugate acid is formed when a proton is transferred to the base. Two substances related in this way are called a conjugate acid–base pair.

The equilibrium expression for the dissociation of an acid in water is

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

where H_3O^+ is simplified to H^+ , $[\text{H}_2\text{O}]$ is not included because it is assumed to be constant, and K_a is called the acid dissociation constant. The strength of an acid is defined by the position of the dissociation (ionization) equilibrium. A small value of K_a denotes a weak acid, one that does not dissociate to any great extent in aqueous solution. A strong acid is one for which the dissociation equilibrium lies far to the right—the K_a value is very large.

Strong acids such as nitric, hydrochloric, sulfuric, and perchloric acids have weak conjugate bases, which have a low affinity for a proton. The strength of an acid is inversely related to the strength of its conjugate base.

Water is an amphoteric substance—it can behave either as an acid or as a base. The autoionization of water demonstrates this property, since one water molecule transfers a proton to another water molecule to produce a hydronium ion and a hydroxide ion:



This leads to the expression

$$K_w = [\text{H}^+][\text{OH}^-]$$

where K_w is called the ion-product constant. It has been experimentally shown that at 25°C in pure water $[\text{H}^+] = [\text{OH}^-] = 1.0 \times 10^{-7} \text{ M}$. Thus, at 25°C ,

$$K_w = 1.0 \times 10^{-14}$$

In an acidic solution, $[\text{H}^+]$ is greater than $[\text{OH}^-]$. In a basic solution, $[\text{OH}^-]$ is greater than $[\text{H}^+]$. In a neutral solution, $[\text{H}^+]$ is equal to $[\text{OH}^-]$.

To describe $[\text{H}^+]$ in aqueous solutions, we often use the pH scale, where

$$\text{pH} = -\log[\text{H}^+]$$

Since pH is a log scale based on 10, the pH changes by 1 for every change by a power of 10 in $[H^+]$. Because pH is defined as $-\log[H^+]$, the pH decreases as $[H^+]$ increases.

The percent dissociation of a weak acid is defined as follows:

$$\text{Percent dissociation} = \frac{\text{amount dissociated (mol/L)}}{\text{initial concentration (mol/L)}} \times 100\%$$

This is another measure of the strength of an acid: The larger the percent dissociation, the stronger the acid. As $[HA]_0$ decreases, $[H^+]$ decreases, but the percent dissociation increases. That is, dilution causes an increase in the percent dissociation.

Strong bases are hydroxide salts, such as NaOH or KOH, that dissociate completely in water. Bases do not have to contain the hydroxide ion; they can be species that remove a proton from water, producing the hydroxide ion. For example, ammonia is a base because it can accept a proton from water:



The equilibrium expression is

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

where K_b always refers to a reaction in which a base reacts with water to produce the conjugate acid and hydroxide ion. Because bases like ammonia must compete with the hydroxide ion for the proton, values of K_b for these bases are typically much less than 1, and these substances are called weak bases.

A polyprotic acid is an acid with more than one acidic proton, which dissociates in a stepwise fashion with a K_a value for each step. Typically, for a weak polyprotic acid,

$$K_{a_1} > K_{a_2} > K_{a_3}$$

Sulfuric acid is unique in that it is a strong acid in the first dissociation step and a weak acid in the second step.

Salts can exhibit neutral, acidic, or basic properties when dissolved in water. Salts that contain the cations of strong bases and the anions of strong acids produce neutral aqueous solutions. A basic solution is produced when the dissolved salt has a neutral cation and an anion that is the conjugate base of a weak acid. An acidic solution is produced when the dissolved salt has a neutral anion and a cation that is the conjugate acid of a weak base. Acidic solutions are also produced by salts containing a highly charged metal cation. For example, the hydrated ion $Al(H_2O)_6^{3+}$ is a weak acid.

Most substances that function as acids or bases contain the $H-O-X$ grouping. Molecules where the $O-X$ is a strong covalent bond tend to behave as acids, especially when X is highly electronegative, because the $H-O$ bond is polarized and weakened. When X has low electronegativity (if X is a metal, for example), the $O-X$ bond tends to be ionic and hydroxide ions form when these substances are dissolved in water.

The Lewis model for acids and bases generalizes the concept of acid-base behavior in terms of electron pairs. A Lewis acid is an electron-pair acceptor, and a Lewis base is an electron-pair donor. The value of the Lewis model is that it covers many reactions that do not involve Brønsted-Lowry acids and bases.

In-Class Discussion Questions

These questions are designed to be considered by groups of students in class. Often these questions work well for introducing a particular topic in class.

1. Consider two beakers of pure water at different temperatures. How do their pH values compare? Which is more acidic? more basic? Explain.
2. Differentiate between the terms *strength* and *concentration* as they apply to acids and bases. When is HCl strong? weak? concentrated? dilute? Answer the same questions for ammonia. Is the conjugate base of a weak acid a strong base?
3. Sketch two graphs: (a) percent dissociation for weak acid HA versus the initial concentration of HA ($[HA]_0$) and (b) H^+ concentration versus $[HA]_0$. Explain both.
4. Consider a solution prepared by mixing a weak acid HA and HCl. What are the major species? Explain what is occurring in solution. How would you calculate the pH? What if you added NaA to this solution? then added NaOH?
5. Explain why salts can be acidic, basic, or neutral, and show examples. Do this without specific numbers.
6. Consider two separate aqueous solutions: one of a weak acid HA and one of HCl. Assuming you started with 10 molecules of each:
 - a. Draw a picture of what each solution looks like at equilibrium.
 - b. What are the major species in each beaker?
 - c. From your pictures, calculate the K_a values of each acid.
 - d. Order the following from the strongest to the weakest base: H_2O , A^- , Cl^- . Explain your order.
7. You are asked to calculate the H^+ concentration in a solution of $NaOH(aq)$. Because sodium hydroxide is a base, can we say there is no H^+ , since having H^+ would imply that the solution is acidic?
8. Consider a solution prepared by mixing a weak acid HA, HCl, and NaA. Which of the following statements best describes what happens?
 - a. The H^+ from the HCl reacts completely with the A^- from the NaA. Then, the HA dissociates somewhat.
 - b. The H^+ from the HCl reacts somewhat with the A^- from the NaA to make HA, while the HA is dissociating. Eventually you have equal amounts of everything.
 - c. The H^+ from the HCl reacts somewhat with the A^- from the NaA to make HA while the HA is dissociating. Eventually all the reactions have equal rates.
 - d. The H^+ from the HCl reacts completely with the A^- from the NaA. Then the HA dissociates somewhat until "too much" H^+ and A^- are formed, so the H^+ and A^- react to form HA, and so on. Eventually equilibrium is reached. Justify your choice, and for choices you did not pick, explain what is wrong with them.

9. Consider a solution formed by mixing 100.0 mL of 0.10 M HA ($K_a = 1.0 \times 10^{-6}$), 100.00 mL of 0.10 M NaA, and 100.0 mL of 0.10 M HCl. In calculating the pH for the final solution, you would make some assumptions about the order in which various reactions occur to simplify the calculations. State these assumptions. Does it matter whether the reactions actually occur in the assumed order? Explain.
10. A certain sodium compound is dissolved in water to liberate Na^+ ions and a certain negative ion. What evidence would you look for to determine whether the anion is behaving as an acid or a base? How could you tell whether the anion is a strong base? Explain how the anion could behave simultaneously as an acid and a base.
11. Acids and bases can be thought of as chemical opposites (acids are proton donors, and bases are proton acceptors). Therefore, one might think that $K_a = 1/K_b$. Why isn't this the case? What is the relationship between K_a and K_b ? Prove it with a derivation.
12. Consider two solutions of the salts $NaX(aq)$ and $NaY(aq)$ at equal concentrations. What would you need to know to determine which solution has the higher pH? Explain how you would decide (perhaps even provide a sample calculation).
13. What is meant by *pH*? True or false: A strong acid solution always has a lower pH than a weak acid solution. Explain.
14. Why is the pH of water at 25°C equal to 7.00?
15. Can the pH of a solution be negative? Explain.

A blue question or exercise number indicates that the answer to that question or exercise appears at the back of this book and a solution appears in the *Solutions Guide*.

Questions

16. Define each of the following using the Arrhenius model.
 - a. strong acid
 - b. strong base
 - c. weak acid
 - d. weak base
17. Define each of the following.
 - a. Arrhenius acid
 - b. Brønsted–Lowry acid
 - c. Lewis acid
 Which of the definitions is most general? Write reactions to justify your answer.
18. Why is H_3O^+ the strongest acid and OH^- the strongest base that can exist in significant amounts in aqueous solutions?
19. Give the conditions for a neutral solution at 25°C, in terms of $[H^+]$, pH, and the relationship between $[H^+]$ and $[OH^-]$.
20. How many significant figures are there in the numbers: 10.78, 6.78, 0.78? If these were pH values, to how many significant figures can you express the $[H^+]$? Explain any discrepancies between your answers to the two questions.
21. The presence of what element most commonly results in basic properties for an organic compound? What is present on this element in compounds that allows it to accept a proton?

22. For oxyacids, how does acid strength depend on
- strength of the bond to the acidic hydrogen atom?
 - electronegativity of the element bonded to the oxygen atom that bears the acidic hydrogen?
 - the number of oxygen atoms?
23. How does the strength of a conjugate base depend on the factors listed in Question 22?
24. In terms of orbitals and electron arrangements, what must be present for a molecule or an ion to act as a Lewis acid? What must be present for a molecule or an ion to act as a Lewis base?
25. Consider the reaction of acetic acid in water
- $$\text{CH}_3\text{CO}_2\text{H}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{CH}_3\text{CO}_2^-(aq) + \text{H}_3\text{O}^+(aq)$$
- where $K_a = 1.8 \times 10^{-5}$.
- Which two bases are competing for the proton?
 - Which is the stronger base?
 - In light of your answer to b, why do we classify the acetate ion (CH_3CO_2^-) as a weak base? Use an appropriate reaction to justify your answer.
26. In general, as base strength increases, conjugate acid strength decreases. Explain why the conjugate acid of the weak base NH_3 is a weak acid.
27. What types of measurements, other than pH measurements, can be made to determine the extent of dissociation of an acid in water?
28. Derive an expression for the relationship between $\text{p}K_a$ and $\text{p}K_b$ for a conjugate acid–base pair. ($\text{p}K = -\log K$.)

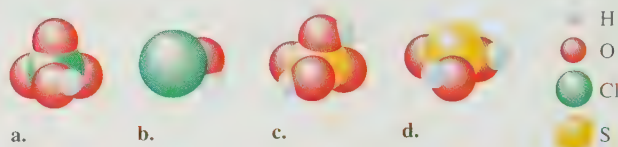
Exercises

In this section similar exercises are paired.

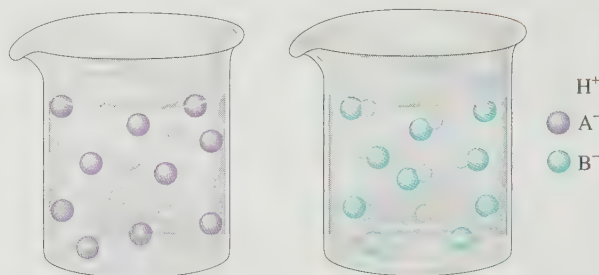
Nature of Acids and Bases

29. Write balanced equations that describe the following reactions.
- the dissociation of perchloric acid in water
 - the dissociation of propanoic acid ($\text{CH}_3\text{CH}_2\text{CO}_2\text{H}$) in water
 - the dissociation of ammonium ion in water
30. Write the dissociation reaction and the corresponding K_a equilibrium expression for each of the following acids in water.
- $\text{HC}_2\text{H}_3\text{O}_2$
 - $\text{Co}(\text{H}_2\text{O})_6^{3+}$
 - CH_3NH_3^+
31. For each of the following aqueous reactions, identify the acid, the base, the conjugate base, and the conjugate acid.
- $\text{HF} + \text{H}_2\text{O} \rightleftharpoons \text{F}^- + \text{H}_3\text{O}^+$
 - $\text{H}_2\text{SO}_4 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{HSO}_4^-$
 - $\text{HSO}_4^- + \text{H}_2\text{O} \rightleftharpoons \text{SO}_4^{2-} + \text{H}_3\text{O}^+$
32. For each of the following aqueous reactions, identify the acid, the base, the conjugate base, and the conjugate acid.
- $\text{Al}(\text{H}_2\text{O})_6^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{Al}(\text{H}_2\text{O})_5(\text{OH})^{2+}$
 - $\text{H}_2\text{O} + \text{HONH}_3^+ \rightleftharpoons \text{HONH}_2 + \text{H}_3\text{O}^+$
 - $\text{HOCl} + \text{C}_6\text{H}_5\text{NH}_2 \rightleftharpoons \text{OCl}^- + \text{C}_6\text{H}_5\text{NH}_3^+$

33. Classify each of the following as a strong acid or a weak acid.



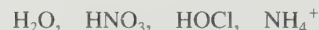
34. Consider the following illustrations:



Which beaker best illustrates what happens when the following acids are dissolved in water?

- HNO_2
- HNO_3
- HCl
- HF
- $\text{HC}_2\text{H}_3\text{O}_2$

35. Use Table 14.2 to order the following from the strongest to the weakest acid.



36. Use Table 14.2 to order the following from the strongest to the weakest base.



37. You may need Table 14.2 to answer the following questions.
- Which is the stronger acid, HCl or H_2O ?
 - Which is the stronger acid, H_2O or HNO_2 ?
 - Which is the stronger acid, HCN or HOC_6H_5 ?
38. You may need Table 14.2 to answer the following questions.
- Which is the stronger base, Cl^- or H_2O ?
 - Which is the stronger base, H_2O or NO_2^- ?
 - Which is the stronger base, CN^- or OC_6H_5^- ?

Autoionization of Water and the pH Scale

39. Calculate the $[\text{OH}^-]$ of each of the following solutions at 25°C . Identify each solution as neutral, acidic, or basic.
- $[\text{H}^+] = 1.0 \times 10^{-7} \text{ M}$
 - $[\text{H}^+] = 6.7 \times 10^{-4} \text{ M}$
 - $[\text{H}^+] = 1.9 \times 10^{-11} \text{ M}$
 - $[\text{H}^+] = 2.3 \text{ M}$
40. Calculate the $[\text{H}^+]$ of each of the following solutions at 25°C . Identify each solution as neutral, acidic, or basic.
- $[\text{OH}^-] = 3.6 \text{ M}$
 - $[\text{OH}^-] = 9.7 \times 10^{-9} \text{ M}$
 - $[\text{OH}^-] = 2.2 \times 10^{-3} \text{ M}$
 - $[\text{OH}^-] = 1.0 \times 10^{-7} \text{ M}$

41. Values of K_w as a function of temperature are as follows:

Temperature (°C)	K_w
0	1.14×10^{-15}
25	1.00×10^{-14}
35	2.09×10^{-14}
40.	2.92×10^{-14}
50.	5.47×10^{-14}

- a. Is the autoionization of water exothermic or endothermic?
b. Calculate $[H^+]$ and $[OH^-]$ in a neutral solution at 50°C.
42. At 40°C, the value of K_w is 2.92×10^{-14} .
a. Calculate the $[H^+]$ and $[OH^-]$ in pure water at 40°C.
b. What is the pH of pure water at 40°C?
c. If the hydroxide ion concentration in a solution is 0.10 M, what is the pH at 40°C?
43. Calculate the pH and pOH of the solutions in Exercises 39 and 40.
44. Calculate $[H^+]$ and $[OH^-]$ for each solution at 25°C. Identify each solution as neutral, acidic, or basic.
a. pH = 7.40 (the normal pH of blood)
b. pH = 15.3
c. pH = -1.0
d. pH = 3.20
e. pOH = 5.0
f. pOH = 9.60
45. The pH of a sample of milk is 6.77 at 25°C. Calculate the pOH, $[H^+]$, and $[OH^-]$ for this sample. Is milk acidic or basic?
46. The pOH of a sample of baking soda dissolved in water is 5.74 at 25°C. Calculate the pH, $[H^+]$, and $[OH^-]$ for this sample. Is the solution acidic or basic?

Solutions of Acids

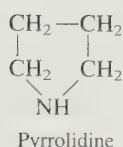
47. What are the major species present in 0.250 M solutions of each of the following acids? Calculate the pH of each of these solutions.
a. $HClO_4$ b. HNO_3
48. Calculate the pH of each of the following solutions of a strong acid in water.
a. 0.10 M HCl c. 1.0×10^{-11} M HCl
b. 5.0 M HCl
49. A solution is prepared by adding 50.0 mL of 0.050 M HCl to 150.0 mL of 0.10 M HNO_3 . Calculate the concentrations of all species in this solution.
50. A solution is prepared by mixing 90.0 mL of 5.00 M HCl and 30.0 mL of 8.00 M HNO_3 . Water is then added until the final volume is 1.00 L. Calculate $[H^+]$, $[OH^-]$, and the pH for this solution.
51. Calculate the concentration of an aqueous HCl solution that has pH = 2.50.
52. Calculate the concentration of an aqueous HNO_3 solution that has pH = 5.10.
53. What are the major species present in 0.250 M solutions of each of the following acids? Calculate the pH of each of these solutions.
a. HNO_2 b. CH_3CO_2H ($HC_2H_3O_2$)
54. What are the major species present in 0.250 M solutions of each of the following acids? Calculate the pH of each of these solutions.
a. HOC_6H_5 b. HCN
55. A solution with a total volume of 250.0 mL is prepared by diluting 20.0 mL of glacial acetic acid with water. Calculate $[H^+]$ and the pH of this solution. Assume that glacial acetic acid is pure liquid acetic acid with a density of 1.05 g/cm³.
56. For propanoic acid ($HC_3H_5O_2$, $K_a = 1.3 \times 10^{-5}$), determine the concentration of all species present, the pH, and the percent dissociation of a 0.100 M solution.
57. Calculate the concentration of all species present and the pH of a 0.020 M HF solution.
58. Calculate the pH of a 0.20 M solution of iodic acid (HIO_3 , $K_a = 0.17$).
59. Monochloroacetic acid, $HC_2H_2ClO_2$, is a skin irritant that is used in "chemical peels" intended to remove the top layer of dead skin from the face and ultimately improve the complexion. The value of K_a for monochloroacetic acid is 1.35×10^{-3} . Calculate the pH of a 0.10 M solution of monochloroacetic acid.
60. Calculate the percent dissociation for a 0.22 M solution of chlorous acid ($HClO_2$, $K_a = 1.2 \times 10^{-2}$).
61. Calculate the pH of each of the following.
a. a solution containing 0.10 M HCl and 0.10 M HOC_6H_5
b. a solution containing 0.050 M HNO_3 and 0.50 M $HC_2H_3O_2$.
62. Calculate the pH of a solution that contains 1.0 M HF and 1.0 M HOC_6H_5 . Also calculate the concentration of $OC_6H_5^-$ in this solution at equilibrium.
63. Calculate the percent dissociation of the acid in each of the following solutions.
a. 0.50 M acetic acid
b. 0.050 M acetic acid
c. 0.0050 M acetic acid
d. Use Le Châtelier's principle to explain why percent dissociation increases as the concentration of a weak acid decreases.
e. Even though the percent dissociation increases from solutions a to c, the $[H^+]$ decreases. Explain.
64. Using the K_a values in Table 14.2, calculate the percent dissociation in a 0.20 M solution of each of the following acids.

- a. nitric acid (HNO_3)
 - b. nitrous acid (HNO_2)
 - c. phenol (HOC_6H_5)
 - d. How is percent dissociation of an acid related to the K_a value for the acid (assuming equal initial concentrations of acids)?
-
65. A 0.15 M solution of a weak acid is 3.0% dissociated. Calculate K_a .
66. In a 0.100 M solution of HF , the percent dissociation is 8.1%. Calculate K_a .
-
67. The pH of a $1.00 \times 10^{-2} M$ solution of cyanic acid (HOCN) is 2.77 at 25°C . Calculate K_a for HOCN from this result.
68. Trichloroacetic acid ($\text{CCl}_3\text{CO}_2\text{H}$) is a corrosive acid that is used to precipitate proteins. The pH of a 0.050 M solution of trichloroacetic acid is the same as the pH of a 0.040 M HClO_4 solution. Calculate K_a for trichloroacetic acid.
-
69. A solution of formic acid (HCOOH , $K_a = 1.8 \times 10^{-4}$) has a pH of 2.70. Calculate the initial concentration of formic acid in this solution.
70. One mole of a weak acid HA was dissolved in 2.0 L of water. After the system had come to equilibrium, the concentration of HA was found to be 0.45 M . Calculate K_a for HA .

Solutions of Bases

71. Write the reaction and the corresponding K_b equilibrium expression for each of the following substances acting as bases in water.
a. NH_3 b. $\text{C}_5\text{H}_5\text{N}$
72. Write the reaction and the corresponding K_b equilibrium expression for each of the following substances acting as bases in water.
a. aniline, $\text{C}_6\text{H}_5\text{NH}_2$ b. dimethylamine, $(\text{CH}_3)_2\text{NH}$
73. Use Table 14.3 to help order the following bases from strongest to weakest.
 NO_3^- , H_2O , NH_3 , $\text{C}_5\text{H}_5\text{N}$
74. Use Table 14.3 to help order the following acids from strongest to weakest.
 HNO_3 , H_2O , NH_4^+ , $\text{C}_5\text{H}_5\text{NH}^+$
75. Use Table 14.3 to help answer the following questions.
a. Which is the stronger base, NO_3^- or NH_3 ?
b. Which is the stronger base, H_2O or NH_3 ?
c. Which is the stronger base, OH^- or NH_3 ?
d. Which is the stronger base, NH_3 or CH_3NH_2 ?
76. Use Table 14.3 to help answer the following questions.
a. Which is the stronger acid, HNO_3 or NH_4^+ ?
b. Which is the stronger acid, H_2O or NH_4^+ ?
c. Which is the stronger acid, NH_4^+ or CH_3NH_3^+ ?
77. Calculate the pH of the following solutions.
a. 0.10 M NaOH c. 2.0 M NaOH
b. $1.0 \times 10^{-10} M$ NaOH
78. Calculate $[\text{OH}^-]$, pOH, and pH for each of the following.
a. 0.00040 M $\text{Ca}(\text{OH})_2$
b. a solution containing 25 g of KOH per liter
c. a solution containing 150.0 g of NaOH per liter
79. What are the major species present in 0.015 M solutions of each of the following bases?
a. KOH b. $\text{Ba}(\text{OH})_2$
What is $[\text{OH}^-]$ and the pH of each of these solutions?
80. What are the major species present in the following mixtures of bases?
a. 0.050 M NaOH and 0.050 M LiOH
b. 0.0010 M $\text{Ba}(\text{OH})_2$ and 0.020 M RbOH
What is $[\text{OH}^-]$ and the pH of each of these solutions?
81. Calculate the concentration of an aqueous KOH solution that has pH = 10.50.
82. Calculate the concentration of an aqueous $\text{Sr}(\text{OH})_2$ that has pH = 10.50.
83. What are the major species present in a 0.150 M NH_3 solution? Calculate the $[\text{OH}^-]$ and the pH of this solution.
84. For the reaction of hydrazine (N_2H_4) in water,
$$\text{H}_2\text{NNH}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{NNH}_3^+(aq) + \text{OH}^-(aq)$$

 K_b is 3.0×10^{-6} . Calculate the concentrations of all species and the pH of a 2.0 M solution of hydrazine in water.
85. Calculate $[\text{OH}^-]$, $[\text{H}^+]$, and the pH of 0.20 M solutions of each of the following amines.
a. Triethylamine $[(\text{C}_2\text{H}_5)_3\text{N}]$, $K_b = 4.0 \times 10^{-4}$
b. Hydroxylamine (HONH_2 , $K_b = 1.1 \times 10^{-8}$)
86. Calculate $[\text{OH}^-]$, $[\text{H}^+]$, and the pH of 0.20 M solutions of each of the following amines (the K_b values are found in Table 14.3).
a. aniline b. pyridine
87. Calculate the pH of a 0.20 M $\text{C}_2\text{H}_5\text{NH}_2$ solution ($K_b = 5.6 \times 10^{-4}$).
88. Calculate the pH of a 0.050 M $(\text{C}_2\text{H}_5)_2\text{NH}$ solution ($K_b = 1.3 \times 10^{-3}$).
89. Calculate the percent ionization in each of the following solutions.
a. 0.10 M NH_3 b. 0.010 M NH_3
90. Calculate the percent ionization in each of the following solutions (see Table 14.3 for K_b values).
a. 0.10 M hydroxylamine (HONH_2 , $K_b = 1.1 \times 10^{-8}$)
b. 0.10 M methylamine (CH_3NH_2)
91. Codeine ($\text{C}_{18}\text{H}_{21}\text{NO}_3$) is a derivative of morphine that is used as an analgesic, narcotic, or antitussive. It was once commonly used in cough syrups but is now available only by prescription because of its addictive properties. If the pH of a $1.7 \times 10^{-3} M$ solution of codeine is 9.59, calculate K_b .
92. The pH of a $1.00 \times 10^{-3} M$ solution of pyrrolidine is 10.82. Calculate K_b .



Polyprotic Acids

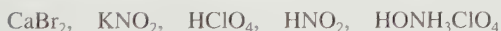
93. Write out the stepwise K_a reactions for the diprotic acid H_2SO_3 .
94. Write out the stepwise K_a reactions for citric acid ($\text{H}_3\text{C}_6\text{H}_5\text{O}_7$), a triprotic acid.
95. Using the K_a values in Table 14.4 and only the first dissociation step, calculate the pH of 0.10 M solutions of each of the following polyprotic acids.
 - a. H_3PO_4 b. H_2CO_3
96. Arsenic acid (H_3AsO_4) is a triprotic acid with $K_{a_1} = 5 \times 10^{-3}$, $K_{a_2} = 8 \times 10^{-8}$, and $K_{a_3} = 6 \times 10^{-10}$. Calculate $[\text{H}^+]$, $[\text{OH}^-]$, $[\text{H}_3\text{AsO}_4]$, $[\text{H}_2\text{AsO}_4^-]$, $[\text{HAsO}_4^{2-}]$, and $[\text{AsO}_4^{3-}]$ in a 0.20 M arsenic acid solution.
97. Calculate the pH of a 2.0 M H_2SO_4 solution.
98. Calculate the pH of a $5.0 \times 10^{-3} M$ solution of H_2SO_4 .

Acid–Base Properties of Salts

99. Arrange the following 0.10 M solutions in order of most acidic to most basic.



100. Arrange the following 0.10 M solutions in order from most acidic to most basic. See Appendix 5 for K_a and K_b values.



101. Given that the K_a value for acetic acid is 1.8×10^{-5} and the K_a value for hypochlorous acid is 3.5×10^{-8} , which is the stronger base, OCl^- or $\text{C}_2\text{H}_3\text{O}_2^-$?
102. The K_b values for ammonia and methylamine are 1.8×10^{-5} and 4.4×10^{-4} , respectively. Which is the stronger acid, NH_4^+ or CH_3NH_3^+ ?
103. Sodium azide (NaN_3) is sometimes added to water to kill bacteria. Calculate the concentration of all species in a 0.010 M solution of NaN_3 . The K_a value for hydrazoic acid (HN_3) is 1.9×10^{-5} .
104. Calculate the concentrations of all species present in a 0.25 M solution of ethylammonium chloride ($\text{C}_2\text{H}_5\text{NH}_3\text{Cl}$).
105. Calculate the pH of each of the following solutions.
 - a. 0.10 M $\text{CH}_3\text{NH}_3\text{Cl}$ b. 0.050 M NaCN
106. Calculate the pH of each of the following solutions.
 - a. 0.12 M KNO_2 c. 0.40 M NH_4ClO_4
 - b. 0.45 M NaOCl
107. An unknown salt is either NaCN , $\text{NaC}_2\text{H}_3\text{O}_2$, NaF , NaCl , or NaOCl . When 0.100 mol of the salt is dissolved in 1.00 L

of solutions, the pH of the solution is 8.07. What is the identity of the salt?

108. Consider a solution of an unknown salt having the general formula BHCl , where B is one of the weak bases in Table 14.3. A 0.10 M solution of the unknown salt has a pH of 5.82. What is the actual formula of the salt?
109. Calculate the pH of a 0.050 M $\text{Al}(\text{NO}_3)_3$ solution. The K_a value for $\text{Al}(\text{H}_2\text{O})_6^{3+}$ is 1.4×10^{-5} .
110. Calculate the pH of a 0.10 M CoCl_3 solution. The K_a value for $\text{Co}(\text{H}_2\text{O})_6^{3+}$ is 1.0×10^{-5} .
111. Are solutions of the following salts acidic, basic, or neutral? For those that are not neutral, write balanced chemical equations for the reactions causing the solution to be acidic or basic. The relevant K_a and K_b values are found in Tables 14.2 and 14.3.
 - a. NaNO_3 c. $\text{C}_5\text{H}_5\text{NHClO}_4$ e. KOCI
 - b. NaNO_2 d. NH_4NO_2 f. NH_4OCl
112. Are solutions of the following salts acidic, basic, or neutral? For those that are not neutral, write balanced equations for the reactions causing the solution to be acidic or basic. The relevant K_a and K_b values are found in Tables 14.2 and 14.3.
 - a. KCl c. $\text{CH}_3\text{NH}_3\text{Cl}$ e. NH_4F
 - b. $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ d. KF f. $\text{CH}_3\text{NH}_3\text{CN}$

Relationships Between Structure and Strengths of Acids and Bases

113. Place the species in each of the following groups in order of increasing acid strength. Explain the order you chose for each group.
 - a. HIO_3 , HBrO_3 c. HOCl , HOI
 - b. HNO_2 , HNO_3 d. H_3PO_4 , H_3PO_3
114. Place the species in each of the following groups in order of increasing base strength. Give your reasoning in each case.
 - a. IO_3^- , BrO_3^- b. NO_2^- , NO_3^- c. OCl^- , OI^-
115. Place the species in each of the following groups in order of increasing acid strength.
 - a. H_2O , H_2S , H_2Se (bond energies: H—O , 467 kJ/mol; H—S , 363 kJ/mol; H—Se , 276 kJ/mol)
 - b. $\text{CH}_3\text{CO}_2\text{H}$, $\text{FCH}_2\text{CO}_2\text{H}$, $\text{F}_2\text{CHCO}_2\text{H}$, $\text{F}_3\text{CCO}_2\text{H}$
 - c. NH_4^+ , HONH_3^+
 - d. NH_4^+ , PH_4^+ (bond energies: N—H , 391 kJ/mol; P—H , 322 kJ/mol)

Give reasons for the orders you chose.
116. Using your results from Exercise 115, place the species in each of the following groups in order of increasing base strength.
 - a. OH^- , SH^- , SeH^- b. NH_3 , PH_3 c. NH_3 , HONH_2
117. Will the following oxides give acidic, basic, or neutral solutions when dissolved in water? Write reactions to justify your answers.
 - a. CaO b. SO_2 c. Cl_2O

- 118.** Will the following oxides give acidic, basic, or neutral solutions when dissolved in water? Write reactions to justify your answers.

a. Li_2O b. CO_2 c. SrO

Lewis Acids and Bases

- 119.** Identify the Lewis acid and the Lewis base in each of the following reactions.

a. $\text{B}(\text{OH})_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{B}(\text{OH})_4^-(\text{aq}) + \text{H}^+(\text{aq})$
 b. $\text{Ag}^+(\text{aq}) + 2\text{NH}_3(\text{aq}) \rightleftharpoons \text{Ag}(\text{NH}_3)_2^+(\text{aq})$
 c. $\text{BF}_3(\text{g}) + \text{F}^-(\text{aq}) \rightleftharpoons \text{BF}_4^-(\text{aq})$

- 120.** Identify the Lewis acid and the Lewis base in each of the following reactions.

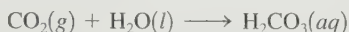
a. $\text{Fe}^{3+}(\text{aq}) + 6\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{Fe}(\text{H}_2\text{O})_6^{3+}(\text{aq})$
 b. $\text{H}_2\text{O}(\text{l}) + \text{CN}^-(\text{aq}) \rightleftharpoons \text{HCN}(\text{aq}) + \text{OH}^-(\text{aq})$
 c. $\text{HgI}_2(\text{s}) + 2\text{I}^-(\text{aq}) \rightleftharpoons \text{HgI}_4^{2-}(\text{aq})$

- 121.** Aluminum hydroxide is an amphoteric substance. It can act as either a Brønsted–Lowry base or a Lewis acid. Write a reaction showing $\text{Al}(\text{OH})_3$ acting as a base toward H^+ and as an acid toward OH^- .

- 122.** Zinc hydroxide is an amphoteric substance. Write equations that describe $\text{Zn}(\text{OH})_2$ acting as a Brønsted–Lowry base toward H^+ and as a Lewis acid toward OH^- .

- 123.** Would you expect Fe^{3+} or Fe^{2+} to be the stronger Lewis acid? Explain.

- 124.** Use the Lewis acid–base model to explain the following reaction.



Additional Exercises

- 125.** A 10.0-mL sample of an HCl solution has a pH of 2.000. What volume of water must be added to change the pH to 4.000?

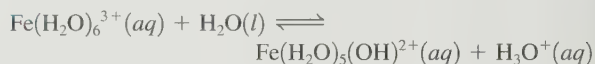
- 126.** Thallium(I) hydroxide is a strong base used in the synthesis of some organic compounds. Calculate the pH of a solution containing 2.48 g TIOH per liter.

- 127.** A solution is tested for pH and conductivity as pictured below:



The solution contains one of the following substances: HCl, NaOH, NH_4Cl , HCN, NH_3 , HF, or NaCN. If the solute concentration is about 1.0 M, what is the identity of the solute?

- 128.** At 25°C, a saturated solution of benzoic acid ($K_a = 6.4 \times 10^{-5}$) has a pH of 2.80. Calculate the water solubility of benzoic acid in moles per liter.
- 129.** A typical vitamin C tablet (containing pure ascorbic acid, $\text{H}_2\text{C}_6\text{H}_6\text{O}_6$) weighs 500. mg. One vitamin C tablet is dissolved in enough water to make 200.0 mL of solution. Calculate the pH of this solution. Ascorbic acid is a diprotic acid.
- 130.** Calculate the pH of an aqueous solution containing $1.0 \times 10^{-2} M$ HCl, $1.0 \times 10^{-2} M$ H_2SO_4 , and $1.0 \times 10^{-2} M$ HCN.
- 131.** Acrylic acid ($\text{CH}_2=\text{CHCO}_2\text{H}$) is a precursor for many important plastics. K_a for acrylic acid is 5.6×10^{-5} .
- a. Calculate the pH of a 0.10 M solution of acrylic acid.
 b. Calculate the percent dissociation of a 0.10 M solution of acrylic acid.
 c. Calculate the pH of a 0.050 M solution of sodium acrylate ($\text{NaC}_3\text{H}_3\text{O}_2$).
- 132.** A 0.20 M sodium chlorobenzoate ($\text{NaC}_7\text{H}_4\text{ClO}_2$) solution has a pH of 8.65. Calculate the pH of a 0.20 M chlorobenzoic acid ($\text{HC}_7\text{H}_4\text{ClO}_2$) solution.
- 133.** The equilibrium constant K_a for the reaction



is 6.0×10^{-3} .

- a. Calculate the pH of a 0.10 M solution of $\text{Fe}(\text{H}_2\text{O})_6^{3+}$.
 b. Will a 1.0 M solution of iron(II) nitrate have a higher or lower pH than a 1.0 M solution of iron(III) nitrate? Explain.
- 134.** Rank the following 0.10 M solutions in order of increasing pH.
- a. HI, HF, NaF, NaI
 b. NH_4Br , HBr, KBr, NH_3
 c. $\text{C}_6\text{H}_5\text{NH}_3\text{NO}_3$, NaNO_3 , NaOH, HOC_6H_5 , KOC_6H_5 , $\text{C}_6\text{H}_5\text{NH}_2$, HNO_3
- 135.** Is an aqueous solution of NaHSO_4 acidic, basic, or neutral? What reaction occurs with water? Calculate the pH of a 0.10 M solution of NaHSO_4 .
- 136.** Calculate $[\text{CO}_3^{2-}]$ in a 0.010 M solution of CO_2 in water (H_2CO_3). If all the CO_3^{2-} in this solution comes from the reaction



what percentage of the H^+ ions in the solution is a result of the dissociation of HCO_3^- ? When acid is added to a solution of sodium hydrogen carbonate (NaHCO_3), vigorous bubbling occurs. How is this reaction related to the existence of carbonic acid (H_2CO_3) molecules in aqueous solution?

- 137.** Hemoglobin (abbreviated Hb) is a protein that is responsible for the transport of oxygen in the blood of mammals. Each hemoglobin molecule contains four iron atoms that are the binding sites for O_2 molecules. The oxygen binding is

pH dependent. The relevant equilibrium reaction is



Use Le Châtelier's principle to answer the following.

- What form of hemoglobin, HbH_4^{4+} or $\text{Hb}(\text{O}_2)_4$, is favored in the lungs? What form is favored in the cells?
- When a person hyperventilates, the concentration of CO_2 in the blood is decreased. How does this affect the oxygen-binding equilibrium? How does breathing into a paper bag help to counteract this effect?
- When a person has suffered a cardiac arrest, injection of a sodium bicarbonate solution is given. Why is this necessary?

138. Calculate the value for the equilibrium constant for each of the following aqueous reactions.

- $\text{NH}_3 + \text{H}_3\text{O}^+ \rightleftharpoons \text{NH}_4^+ + \text{H}_2\text{O}$
- $\text{NO}_2^- + \text{H}_3\text{O}^+ \rightleftharpoons \text{HNO}_2 + \text{H}_2\text{O}$
- $\text{NH}_4^+ + \text{OH}^- \rightleftharpoons \text{NH}_3 + \text{H}_2\text{O}$
- $\text{HNO}_2 + \text{OH}^- \rightleftharpoons \text{H}_2\text{O} + \text{NO}_2^-$

139. Students are often surprised to learn that organic acids, such as acetic acid, contain $-\text{OH}$ groups. Actually, all oxyacids contain hydroxyl groups. Sulfuric acid, usually written as H_2SO_4 , has the structural formula $\text{SO}_2(\text{OH})_2$, where S is the central atom. Identify the acids whose structural formulas are shown below. Why do they behave as acids, while NaOH and KOH are bases?

- $\text{SO}(\text{OH})_2$
- $\text{HPO}(\text{OH})_2$
- $\text{ClO}_2(\text{OH})$

Challenge Problems

140. The pH of $1.0 \times 10^{-8} \text{ M}$ hydrochloric acid is not 8.00. The correct pH can be calculated by considering the relationship between the molarities of the three principal ions in the solution (H^+ , Cl^- , and OH^-). These molarities can be calculated from algebraic equations that can be derived from the considerations given below.

- The solution is electrically neutral.
- The hydrochloric acid can be assumed to be 100% ionized.
- The product of the molarities of the hydronium ions and the hydroxide ions must equal K_w .

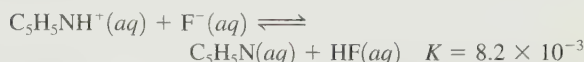
Calculate the pH of a $1.0 \times 10^{-8} \text{ M}$ HCl solution.

141. Calculate the pH of a $1.0 \times 10^{-7} \text{ M}$ solution of NaOH in water.

142. Consider 50.0 mL of a solution of weak acid HA ($K_a = 1.00 \times 10^{-6}$), which has a pH of 4.000. What volume of water must be added to make the pH = 5.000?

143. Making use of the assumptions we ordinarily make in calculating the pH of an aqueous solution of a weak acid, calculate the pH of a $1.0 \times 10^{-6} \text{ M}$ solution of hypobromous acid (HBrO , $K_a = 2 \times 10^{-9}$). What is wrong with your answer? Why is it wrong? Without trying to solve the problem, tell what has to be included to solve the problem correctly.

144. Calculate the pH of a 0.200 M solution of $\text{C}_5\text{H}_5\text{NHF}$. *Hint:* $\text{C}_5\text{H}_5\text{NHF}$ is a salt composed of $\text{C}_5\text{H}_5\text{NH}^+$ and F^- ions. The principal equilibrium in this solution is the best acid reacting with the best base; the reaction for the principal equilibrium is



145. Calculate $[\text{OH}^-]$ in a solution obtained by adding 0.0100 mol of solid NaOH to 1.00 L of 15.0 M NH_3 .

146. A certain acid, HA, has a vapor density of 5.11 g/L when in the gas phase at a temperature of 25°C and a pressure of 1.00 atm. When 1.50 g of this acid is dissolved in enough water to make 100.0 mL of solution, the pH is found to be 1.80. Calculate K_a for the acid.

147. Consider the species PO_4^{3-} , HPO_4^{2-} , and H_2PO_4^- . Each ion can act as a base in water. Determine the K_b value for each of these species. Which species is the strongest base?

148. a. The principal equilibrium in a solution of NaHCO_3 is



Calculate the value of the equilibrium constant for this reaction.

- At equilibrium, what is the relationship between $[\text{H}_2\text{CO}_3]$ and $[\text{CO}_3^{2-}]$?
- Using the equilibrium

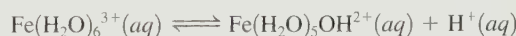


derive an expression for the pH of the solution in terms of K_{a1} and K_{a2} , using the result from part b.

- What is the pH of a solution of NaHCO_3 ?

149. A 0.100-g sample of the weak acid HA (molar mass = 100.0 g/mol) is dissolved in 500.0 g of water. The freezing point of the resulting solution is -0.0056°C . Calculate the value of K_a for this acid. Assume molarity equals molality in this solution.

150. A sample containing 0.0500 mol of $\text{Fe}_2(\text{SO}_4)_3$ is dissolved in enough water to make 1.00 L of solution. This solution contains hydrated SO_4^{2-} and $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ ions. The latter behaves as an acid:



- Calculate the expected osmotic pressure of this solution at 25°C if the above dissociation is negligible.
- The actual osmotic pressure of the solution is 6.73 atm at 25°C . Calculate K_a for the dissociation reaction of $\text{Fe}(\text{H}_2\text{O})_6^{3+}$. (To do this calculation, you must assume that none of the ions goes through the semipermeable membrane. Actually, this is not a great assumption for the tiny H^+ ion.)

Marathon Problem*

This problem is designed to incorporate several concepts and techniques into one situation. Marathon Problems can be used in class by groups of students to help facilitate problem-solving skills.

151. Captain Kirk, of the Starship *Enterprise*, has been told by his superiors that only a chemist can be trusted with the combination to the safe containing the dilithium crystals that power the ship. The combination is the pH of solution A, described below, followed by the pH of solution C. (Example: If the pH of solution A is 3.47 and that of solution C is 8.15, then the combination to the safe is 3-47-8-15.) The chemist must determine the combination using only the information below (all solutions are at 25°C):

Solution A is 50.0 mL of a 0.100 M solution of the weak monoprotic acid HX.

Solution B is a 0.0500 M solution of the salt NaX. It has a pH of 10.02.

Solution C is made by adding 15.0 mL of 0.250 M KOH to solution A.

What is the combination to the safe?

Media Activities

1. Open the Weak and Strong Acid Understanding Concepts activity on the student CD to review differences between strong acids and weak acids. The exercises in this activity allow you to compare major species present at equilibrium for two different acids

and then answer some questions regarding relative acid strength between the two acids. Do several of the exercises until you are proficient at relating major species present to relative acid strength. For the pH question, the solution with the higher pH will be the weaker acid (the acid that has the fewest molecules disassociated).

2. Another way to differentiate strong acids from weak acids is by conductivity experiments. Open the Conductivities of Aqueous Solutions Visualization. Knowing that acetic acid is a weak acid and HCl is a strong acid, predict the relative brightness of the light for the acetic acid solution versus the HCl solution. Play the video to confirm your answer. In terms of major species present at equilibrium, explain why the HCl solution produced a brighter light as compared to the acetic solution.
3. a. Open the Self-Ionization of Water Visualization. The ion product constant, K_w , refers to a specific reaction. What is the K_w reaction? H^+ is commonly used as an abbreviation for what substance? What is the value of K_w at 25°C? Using the value of K_w at 25°C and the K_w expression, why does $[H^+] = [OH^-] = 1.0 \times 10^{-7} M$ in water when neither an acid nor a base is present? What is pH and pOH? Is pH and $[H^+]$ directly or inversely related? For a neutral solution of water, how is pH and pOH related at 25°C?
- b. When a lot of an acid is dissolved in water, how is $[H^+]$ related to $[OH^-]$ and how is pH related to pOH? How does the pH of a 0.10 M strong acid solution compare to the pH of a 0.10 M weak acid solution? When a lot of a base is added to water, how is $[OH^-]$ related to $[H^+]$ and how is pOH related to pH?
4. Test your understanding of Chapter 14 material by taking the ACE quizzes on the student web site.

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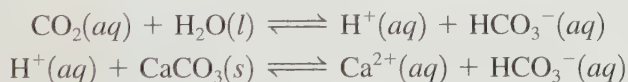
For additional web activities and other resources, visit the Zumdahl, *Chemistry*, Sixth Edition textbook site at <http://chemistry.college.hmco.com/students>.



Applications of Aqueous Equilibria

Much important chemistry, including almost all the chemistry of the natural world, occurs in aqueous solution. We have already introduced one very significant class of aqueous equilibria, acid–base reactions. In this chapter we consider more applications of acid–base chemistry and introduce two additional types of aqueous equilibria, those involving the solubility of salts and those involving the formation of complex ions.

The interplay of acid–base, solubility, and complex ion equilibria is often important in natural processes, such as the weathering of minerals, the uptake of nutrients by plants, and tooth decay. For example, limestone (CaCO_3) will dissolve in water made acidic by dissolved carbon dioxide:



This two-step process and its reverse account for the formation of limestone caves and the stalactites and stalagmites found therein. In the forward direction of the process, the acidic water (containing carbon dioxide) dissolves the underground limestone deposits, thereby forming a cavern. The reverse process occurs as the water drips from the ceiling of the cave, and the carbon dioxide is lost to the air. This causes solid calcium carbonate to form, producing stalactites on the ceiling and stalagmites where the drops hit the cave floor.

Before we consider the other types of aqueous equilibria, we will deal with acid–base equilibria in more detail.

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- Equilibrium Calculations

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15.6 Solubility Equilibria and the Solubility Product

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- Complex Ions and Solubility

Stalactites are formed when carbonate minerals dissolve in ground water acidified by carbon dioxide and then solidify when the water evaporates.

Acid–Base Equilibria

15.1 Solutions of Acids or Bases Containing a Common Ion

In Chapter 14 we were concerned with calculating the equilibrium concentrations of species (particularly H^+ ions) in solutions containing an acid or a base. In this section we discuss solutions that contain not only the weak acid HA but also its salt NaA. Although this appears to be a new type of problem, we will see that this case can be handled rather easily using the procedures developed in Chapter 14.

Suppose we have a solution containing the weak acid hydrofluoric acid (HF, $K_a = 7.2 \times 10^{-4}$) and its salt sodium fluoride (NaF). Recall that when a salt dissolves in water, it breaks up completely into its ions—it is a strong electrolyte:

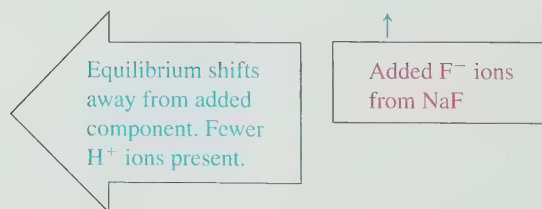


Since hydrofluoric acid is a weak acid and only slightly dissociated, the major species in the solution are HF, Na^+ , F^- , and H_2O . The **common ion** in this solution is F^- , since it is produced by both hydrofluoric acid and sodium fluoride. What effect does the presence of the dissolved sodium fluoride have on the dissociation equilibrium of hydrofluoric acid?

To answer this question, we compare the extent of dissociation of hydrofluoric acid in two different solutions, the first containing 1.0 M HF and the second containing 1.0 M HF and 1.0 M NaF. By Le Châtelier's principle, we would expect the dissociation equilibrium for HF



in the second solution to be *driven to the left by the presence of F^- ions from the NaF*. Thus the extent of dissociation of HF will be *less* in the presence of dissolved NaF:



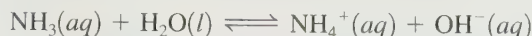
The common ion effect is an application of Le Châtelier's principle.

The shift in equilibrium position that occurs because of the addition of an ion already involved in the equilibrium reaction is called the **common ion effect**. This effect makes a solution of NaF and HF less acidic than a solution of HF alone.

The common ion effect is quite general. For example, solid NH_4Cl added to a 1.0 M NH_3 solution produces additional ammonium ions:



and this causes the position of the ammonia–water equilibrium to shift to the left:



This reduces the equilibrium concentration of OH^- ions.

The common ion effect is also important in solutions of polyprotic acids. The production of protons by the first dissociation step greatly inhibits the succeeding dissociation steps, which, of course, also produce protons, the common ion in this case. We will see later in this chapter that the common ion effect is also important in dealing with the solubility of salts.

Equilibrium Calculations

The procedures for finding the pH of a solution containing a weak acid or base plus a common ion are very similar to the procedures, which we covered in Chapter 14, for solutions containing the acids or bases alone. For example, in the case of a weak acid, the only important difference is that the initial concentration of the anion A^- is not zero in a solution that also contains the salt NaA . Sample Exercise 15.1 illustrates a typical example using the same general approach we developed in Chapter 14.

SAMPLE EXERCISE 15.1

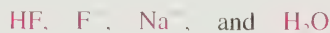
Acidic Solutions Containing Common Ions

In Section 14.5 we found that the equilibrium concentration of H^+ in a 1.0 M HF solution is 2.7×10^{-2} M, and the percent dissociation of HF is 2.7%. Calculate $[\text{H}^+]$ and the percent dissociation of HF in a solution containing 1.0 M HF ($K_a = 7.2 \times 10^{-4}$) and 1.0 M NaF.

SOLUTION

As the aqueous solutions we consider become more complex, it is more important than ever to be systematic and to *focus on the chemistry* occurring in the solution before thinking about mathematical procedures. The way to do this is *always* to write the major species first and consider the chemical properties of each one.

In a solution containing 1.0 M HF and 1.0 M NaF, the major species are

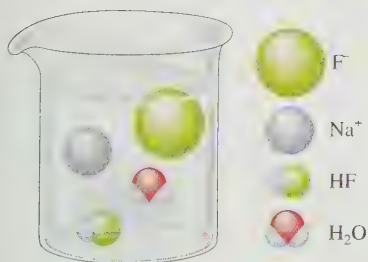


We know that Na^+ ions have neither acidic nor basic properties and that water is a very weak acid (or base). Therefore, the important species are HF and F^- , which participate in the acid dissociation equilibrium that controls $[\text{H}^+]$ in this solution. That is, the position of the equilibrium



will determine $[\text{H}^+]$ in the solution. The equilibrium expression is

$$K_a = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]} = 7.2 \times 10^{-4}$$



The important concentrations are shown in the following table.

Initial Concentration (mol/L)		Equilibrium Concentration (mol/L)
$[\text{HF}]_0 = 1.0$ (from dissolved HF)	$\xrightarrow{x \text{ mol/L HF dissociates}}$	$[\text{HF}] = 1.0 - x$
$[\text{F}^-]_0 = 1.0$ (from dissolved NaF)		$[\text{F}^-] = 1.0 + x$
$[\text{H}^+]_0 = 0$ (neglect contribution from H_2O)		$[\text{H}^+] = x$

Note that $[\text{F}^-]_0 = 1.0 \text{ M}$ because of the dissolved sodium fluoride and that at equilibrium $[\text{F}^-] > 1.0 \text{ M}$ because when the acid dissociates it produces F^- as well as H^+ . Then

$$K_a = 7.2 \times 10^{-4} = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]} = \frac{(x)(1.0 + x)}{1.0 - x} \approx \frac{(x)(1.0)}{1.0}$$

(since x is expected to be small).

Solving for x gives

$$x = \frac{1.0}{1.0}(7.2 \times 10^{-4}) = 7.2 \times 10^{-4}$$

Noting that x is small compared to 1.0, we conclude that this result is acceptable. Thus

$$[\text{H}^+] = x = 7.2 \times 10^{-4} \text{ M} \quad (\text{The pH is 3.14.})$$

The percent dissociation of HF in this solution is

$$\frac{[\text{H}^+]}{[\text{HF}]_0} \times 100 = \frac{7.2 \times 10^{-4} \text{ M}}{1.0 \text{ M}} \times 100 = 0.072\%$$

Compare these values for $[\text{H}^+]$ and percent dissociation of HF with those for a 1.0 M HF solution, where $[\text{H}^+] = 2.7 \times 10^{-2} \text{ M}$ and the percent dissociation is 2.7%. The large difference shows clearly that the presence of the F^- ions from the dissolved NaF greatly inhibits the dissociation of HF. The position of the acid dissociation equilibrium has been shifted to the left by the presence of F^- ions from NaF.

See Exercises 15.25 and 15.26.

15.2 Buffered Solutions



Understanding Concepts: Buffers

The most important buffering system in the blood involves HCO_3^- and H_2CO_3 .

The most important application of acid–base solutions containing a common ion is for buffering. A **buffered solution** is one that *resists a change in its pH* when either hydroxide ions or protons are added. The most important practical example of a buffered solution is our blood, which can absorb the acids and bases produced in biologic reactions without changing its pH. A constant pH for blood is vital because cells can survive only in a very narrow pH range.

The systematic approach developed in Chapter 14 for weak acids and bases applies to buffered solutions.

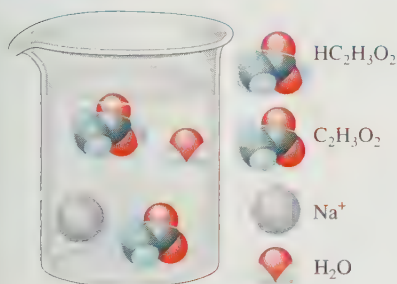
A buffered solution may contain a *weak* acid and its salt (for example, HF and NaF) or a *weak* base and its salt (for example, NH_3 and NH_4Cl). By choosing the appropriate components, a solution can be buffered at virtually any pH.

In treating buffered solutions in this chapter, we will start by considering the equilibrium calculations. We will then use these results to show how buffering works. That is, we will answer the question: How does a buffered solution resist changes in pH when an acid or a base is added?

As you do the calculations associated with buffered solutions, keep in mind that these are merely solutions containing weak acids or bases, and the procedures required are the same ones we have already developed. Be sure to use the systematic approach introduced in Chapter 14.

SAMPLE EXERCISE 15.2

Notice as you do this problem that it is exactly like examples you have seen in Chapter 14.

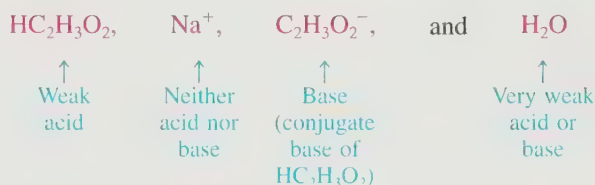


The pH of a Buffered Solution I

A buffered solution contains 0.50 M acetic acid ($\text{HC}_2\text{H}_3\text{O}_2$, $K_a = 1.8 \times 10^{-5}$) and 0.50 M sodium acetate ($\text{NaC}_2\text{H}_3\text{O}_2$). Calculate the pH of this solution.

SOLUTION

The major species in the solution are



Examination of the solution components leads to the conclusion that the acetic acid dissociation equilibrium, which involves both $\text{HC}_2\text{H}_3\text{O}_2$ and $\text{C}_2\text{H}_3\text{O}_2^-$, will control the pH of the solution:



$$K_a = 1.8 \times 10^{-5} = \frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]}$$

The concentrations are as follows:

Initial Concentration (mol/L)		Equilibrium Concentration (mol/L)
$[\text{HC}_2\text{H}_3\text{O}_2]_0 = 0.50$	x mol/L of $\text{HC}_2\text{H}_3\text{O}_2$ dissociates to reach equilibrium	$[\text{HC}_2\text{H}_3\text{O}_2] = 0.50 - x$
$[\text{C}_2\text{H}_3\text{O}_2^-]_0 = 0.50$		$[\text{C}_2\text{H}_3\text{O}_2^-] = 0.50 + x$
$[\text{H}^+]_0 \approx 0$		$[\text{H}^+] = x$

The corresponding ICE table is:

	$\text{HC}_2\text{H}_3\text{O}_2(aq)$	$\rightleftharpoons$	$\text{H}^+(aq)$	+	$\text{C}_2\text{H}_3\text{O}_2^-(aq)$
Initial:	0.50		≈ 0		0.50
Change:	$-x$		$+x$		$+x$
Equilibrium:	$0.50 - x$		x		$0.50 + x$



A digital pH meter shows the pH of the buffered solution to be 4.740.

Then

$$K_a = 1.8 \times 10^{-5} = \frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = \frac{(x)(0.50 + x)}{0.50 - x} \approx \frac{(x)(0.50)}{0.50}$$

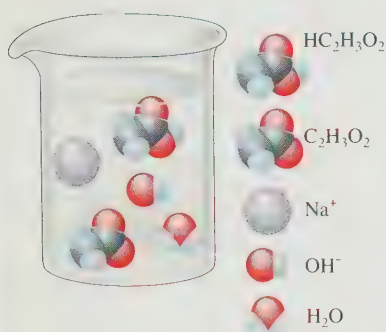
and $x \approx 1.8 \times 10^{-5}$

The approximations are valid (by the 5% rule), so

$$[\text{H}^+] = x = 1.8 \times 10^{-5} \text{ M} \quad \text{and} \quad \text{pH} = 4.74$$

See Exercises 15.33 and 15.34.

SAMPLE EXERCISE 15.3



pH Changes in Buffered Solutions

Calculate the change in pH that occurs when 0.010 mol solid NaOH is added to 1.0 L of the buffered solution described in Sample Exercise 15.2. Compare this pH change with that which occurs when 0.010 mol solid NaOH is added to 1.0 L of water.

SOLUTION

Since the added solid NaOH will completely dissociate, the major species in solution *before any reaction occurs* are $\text{HC}_2\text{H}_3\text{O}_2$, Na^+ , $\text{C}_2\text{H}_3\text{O}_2^-$, OH^- , and H_2O . Note that the solution contains a relatively large amount of the very strong base hydroxide ion, which has a great affinity for protons. The best source of protons is the acetic acid, and the reaction that will occur is



Although acetic acid is a weak acid, the hydroxide ion is such a strong base that the reaction above will *proceed essentially to completion* (until the OH^- ions are consumed).

The best approach to this problem involves two distinct steps: (1) assume that the reaction goes to completion, and carry out the stoichiometric calculations, and then (2) carry out the equilibrium calculations.

1. *The stoichiometry problem.* The stoichiometry for the reaction is shown below.

	$\text{HC}_2\text{H}_3\text{O}_2$	+	OH^-	$\longrightarrow$	$\text{C}_2\text{H}_3\text{O}_2^-$	+	H_2O
Before	1.0 L $\times$ 0.50 M		0.010 mol		1.0 L $\times$ 0.50 M		
reaction:	= 0.50 mol				= 0.50 mol		
After	0.50 - 0.010		0.010 - 0.010		0.50 + 0.010		
reaction:	= 0.49 mol		= 0 mol		= 0.51 mol		

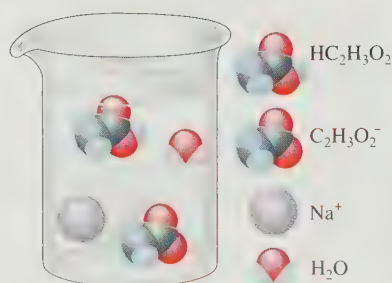
Note that 0.010 mol $\text{HC}_2\text{H}_3\text{O}_2$ has been converted to 0.010 mol $\text{C}_2\text{H}_3\text{O}_2^-$ by the added OH^- .

2. *The equilibrium problem.* After the reaction between OH^- and $\text{HC}_2\text{H}_3\text{O}_2$ is complete, the major species in solution are



The dominant equilibrium involves the dissociation of acetic acid.

This problem is then very similar to that in Sample Exercise 15.2. The only difference is that the addition of 0.010 mol OH^- has consumed some $\text{HC}_2\text{H}_3\text{O}_2$ and produced some $\text{C}_2\text{H}_3\text{O}_2^-$, yielding the following ICE table:





(top) Pure water at pH 7.000.
(bottom) When 0.01 mol NaOH is added to 1.0 L of pure water, the pH jumps to 12.000.

	$\text{HC}_2\text{H}_3\text{O}_2(aq)$	$\rightleftharpoons$	$\text{H}^+(aq)$	+	$\text{C}_2\text{H}_3\text{O}_2^-(aq)$
Initial:	0.49		0		0.51
Change:	$-x$		$+x$		$+x$
Equilibrium:	$0.49 - x$		x		$0.51 + x$

Note that the initial concentrations are defined after the reaction with OH^- is complete but before the system adjusts to equilibrium. Following the usual procedure gives

$$K_a = 1.8 \times 10^{-5} = \frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = \frac{(x)(0.51 + x)}{0.49 - x} \approx \frac{(x)(0.51)}{0.49}$$

and $x \approx 1.7 \times 10^{-5}$

The approximations are valid (by the 5% rule), so

$$[\text{H}^+] = x = 1.7 \times 10^{-5} \quad \text{and} \quad \text{pH} = 4.76$$

The change in pH produced by the addition of 0.01 mol OH^- to this buffered solution is then

$$\begin{array}{ccc} 4.76 & - & 4.74 \\ \uparrow & & \uparrow \\ \text{New solution} & & \text{Original solution} \end{array} = +0.02$$

The pH increased by 0.02 pH units.

Now compare this with what happens when 0.01 mol solid NaOH is added to 1.0 L water to give 0.01 M NaOH. In this case $[\text{OH}^-] = 0.01 \text{ M}$ and

$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-2}} = 1.0 \times 10^{-12}$$

$$\text{pH} = 12.00$$

Thus the change in pH is

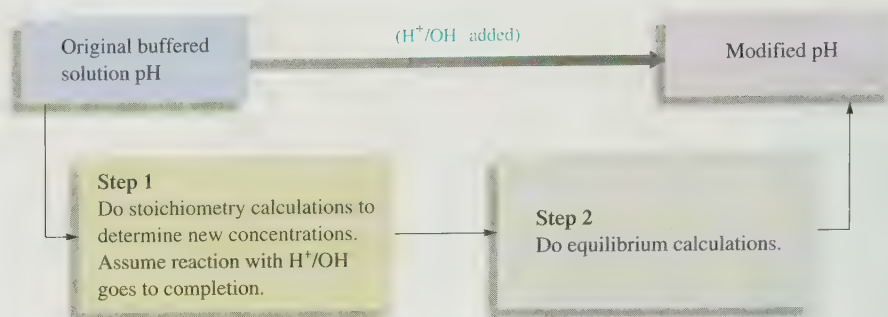
$$\begin{array}{ccc} 12.00 & - & 7.00 \\ \uparrow & & \uparrow \\ \text{New solution} & & \text{Pure water} \end{array} = +5.00$$

The increase is 5.00 pH units. Note how well the buffered solution resists a change in pH as compared with pure water.

See Exercises 15.35 and 15.36.

Sample Exercises 15.2 and 15.3 represent typical buffer problems that involve all the concepts that you need to know to handle buffered solutions containing weak acids. Pay special attention to the following points:

1. Buffered solutions are simply solutions of weak acids or bases containing a common ion. The pH calculations on buffered solutions require exactly the same procedures introduced in Chapter 14. *This is not a new type of problem.*
2. When a strong acid or base is added to a buffered solution, it is best to deal with the stoichiometry of the resulting reaction first. After the stoichiometric calculations are completed, then consider the equilibrium calculations. This procedure can be presented as follows:

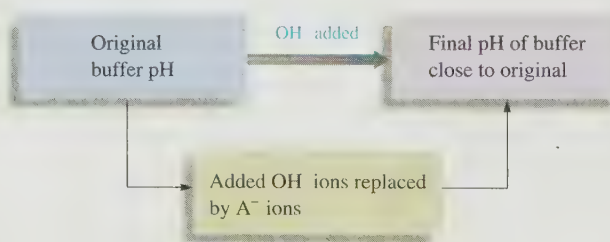


Buffering: How Does It Work?

Sample Exercises 15.2 and 15.3 demonstrate the ability of a buffered solution to absorb hydroxide ions without a significant change in pH. *But how does a buffer work?* Suppose a buffered solution contains relatively large quantities of a weak acid HA and its conjugate base A^- . When hydroxide ions are added to the solution, since the weak acid represents the best source of protons, the following reaction occurs:



The net result is that OH^- ions are not allowed to accumulate but are replaced by A^- ions.



The stability of the pH under these conditions can be understood by examining the equilibrium expression for the dissociation of HA:

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

or, rearranging,

$$[H^+] = K_a \frac{[HA]}{[A^-]}$$

In a buffered solution the pH is governed by the ratio $[HA]/[A^-]$.

In other words, the *equilibrium concentration of H^+ , and thus the pH, is determined by the ratio $[HA]/[A^-]$* . When OH^- ions are added, HA is converted to A^- , and the ratio $[HA]/[A^-]$ decreases. However, *if the amounts of HA and A^- originally present are very large compared with the amount of OH^- added, the change in the $[HA]/[A^-]$ ratio will be small.*

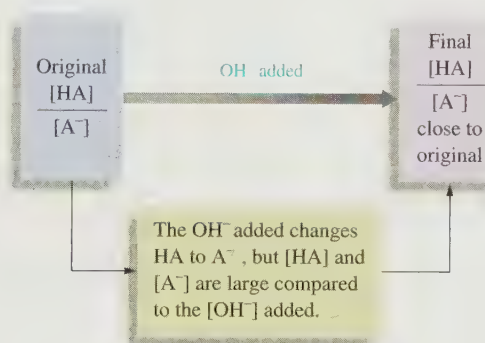
In Sample Exercises 15.2 and 15.3,

$$\frac{[\text{HA}]}{[\text{A}^-]} = \frac{0.50}{0.50} = 1.0 \quad \text{Initially}$$

$$\frac{[\text{HA}]}{[\text{A}^-]} = \frac{0.49}{0.51} = 0.96 \quad \text{After adding 0.01 mol/L OH}^-$$

The change in the ratio $[\text{HA}]/[\text{A}^-]$ is very small. Thus the $[\text{H}^+]$ and the pH remain essentially constant.

The essence of buffering, then, is that $[\text{HA}]$ and $[\text{A}^-]$ are large compared with the amount of OH^- added. Thus, when the OH^- is added, the concentrations of HA and A^- change, but only by small amounts. Under these conditions, the $[\text{HA}]/[\text{A}^-]$ ratio and thus the $[\text{H}^+]$ remain virtually constant.



Similar reasoning applies when protons are added to a buffered solution of a weak acid and a salt of its conjugate base. Because the A^- ion has a high affinity for H^+ , the added H^+ ions react with A^- to form the weak acid:



and free H^+ ions do not accumulate. In this case there will be a net change of A^- to HA. However, if $[\text{A}^-]$ and $[\text{HA}]$ are large compared with the $[\text{H}^+]$ added, little change in the pH will occur.

The form of the acid dissociation equilibrium expression

$$[\text{H}^+] = K_a \frac{[\text{HA}]}{[\text{A}^-]} \quad (15.1)$$

is often useful for calculating $[\text{H}^+]$ in a buffered solution, since $[\text{HA}]$ and $[\text{A}^-]$ are known. For example, to calculate $[\text{H}^+]$ in a buffered solution containing 0.10 M HF ($K_a = 7.2 \times 10^{-4}$) and 0.30 M NaF, we simply substitute into Equation (15.1):

$$[\text{H}^+] = \overset{[\text{HF}]}{\underset{\substack{\nearrow K_a \\ \nwarrow [\text{F}^-]}}{(7.2 \times 10^{-4})}} \frac{0.10}{0.30} = 2.4 \times 10^{-4} \text{ M}$$

Another useful form of Equation (15.1) can be obtained by taking the negative log of both sides:

$$-\log[\text{H}^+] = -\log(K_a) - \log\left(\frac{[\text{HA}]}{[\text{A}^-]}\right)$$

That is,
$$\text{pH} = \text{p}K_a - \log\left(\frac{[\text{HA}]}{[\text{A}^-]}\right)$$

or, where inverting the log term reverses the sign:

$$\text{pH} = \text{p}K_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right) = \text{p}K_a + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right) \quad (15.2)$$

This log form of the expression for K_a is called the **Henderson–Hasselbalch equation** and is useful for calculating the pH of solutions when the ratio $[\text{HA}]/[\text{A}^-]$ is known.

For a particular buffering system (acid–conjugate base pair), all solutions that have the same ratio $[\text{A}^-]/[\text{HA}]$ will have the same pH. For example, a buffered solution containing 5.0 M $\text{HC}_2\text{H}_3\text{O}_2$ and 3.0 M $\text{NaC}_2\text{H}_3\text{O}_2$ will have the same pH as one containing 0.050 M $\text{HC}_2\text{H}_3\text{O}_2$ and 0.030 M $\text{NaC}_2\text{H}_3\text{O}_2$. This can be shown as follows:

System	$[\text{A}^-]/[\text{HA}]$
5.0 M $\text{HC}_2\text{H}_3\text{O}_2$ and 3.0 M $\text{NaC}_2\text{H}_3\text{O}_2$	$\frac{3.0 \text{ M}}{5.0 \text{ M}} = 0.60$
0.050 M $\text{HC}_2\text{H}_3\text{O}_2$ and 0.030 M $\text{NaC}_2\text{H}_3\text{O}_2$	$\frac{0.030 \text{ M}}{0.050 \text{ M}} = 0.60$

Therefore,

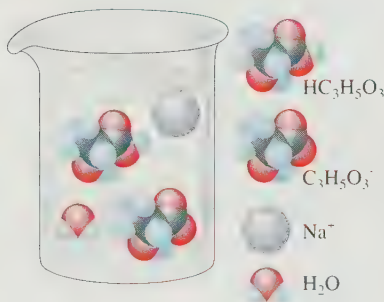
$$\text{pH} = \text{p}K_a + \log\left(\frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]}\right) = 4.74 + \log(0.60) = 4.74 - 0.22 = 4.52$$

Note that in using this equation we have assumed that the equilibrium concentrations of A^- and HA are equal to the initial concentrations. That is, we are assuming the validity of the approximations

$$[\text{A}^-] = [\text{A}^-]_0 + x \approx [\text{A}^-]_0 \quad \text{and} \quad [\text{HA}] = [\text{HA}]_0 - x \approx [\text{HA}]_0$$

where x is the amount of acid that dissociates. Since the initial concentrations of HA and A^- are relatively large in a buffered solution, this assumption is generally acceptable.

SAMPLE EXERCISE 15.4



The pH of a Buffered Solution II

Calculate the pH of a solution containing 0.75 M lactic acid ($K_a = 1.4 \times 10^{-4}$) and 0.25 M sodium lactate. Lactic acid ($\text{HC}_3\text{H}_5\text{O}_3$) is a common constituent of biologic systems. For example, it is found in milk and is present in human muscle tissue during exertion.

SOLUTION

The major species in solution are



Since Na^+ has no acid–base properties and H_2O is a weak acid or base, the pH will be controlled by the lactic acid dissociation equilibrium:



$$K_a = \frac{[\text{H}^+][\text{C}_3\text{H}_5\text{O}_3^-]}{[\text{HC}_3\text{H}_5\text{O}_3]} = 1.4 \times 10^{-4}$$

Since $[\text{HC}_3\text{H}_5\text{O}_3]_0$ and $[\text{C}_3\text{H}_5\text{O}_3^-]_0$ are relatively large,

$$[\text{HC}_3\text{H}_5\text{O}_3] \approx [\text{HC}_3\text{H}_5\text{O}_3]_0 = 0.75 \text{ M}$$

and

$$[\text{C}_3\text{H}_5\text{O}_3^-] \approx [\text{C}_3\text{H}_5\text{O}_3^-]_0 = 0.25 \text{ M}$$

Thus, using the rearranged K_a expression, we have

$$[\text{H}^+] = K_a \frac{[\text{HC}_3\text{H}_5\text{O}_3]}{[\text{C}_3\text{H}_5\text{O}_3^-]} = (1.4 \times 10^{-4}) \frac{(0.75 \text{ M})}{(0.25 \text{ M})} = 4.2 \times 10^{-4} \text{ M}$$

and

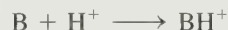
$$\text{pH} = -\log(4.2 \times 10^{-4}) = 3.38$$

Alternatively, we could use the Henderson–Hasselbalch equation:

$$\text{pH} = \text{p}K_a + \log\left(\frac{[\text{C}_3\text{H}_5\text{O}_3^-]}{[\text{HC}_3\text{H}_5\text{O}_3]}\right) = 3.85 + \log\left(\frac{0.25 \text{ M}}{0.75 \text{ M}}\right) = 3.38$$

See Exercises 15.37 and 15.38.

Buffered solutions also can be formed from a weak base and the corresponding conjugate acid. In these solutions, the weak base B reacts with any H^+ added:

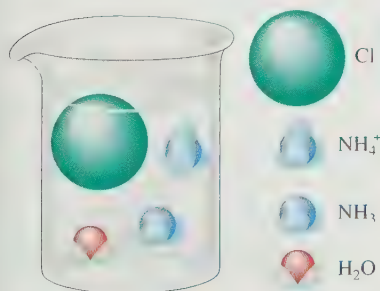


and the conjugate acid BH^+ reacts with any added OH^- :



The approach needed to perform pH calculations for these systems is virtually identical to that used above. This makes sense because, as is true of all buffered solutions, a weak acid (BH^+) and a weak base (B) are present. A typical case is illustrated in Sample Exercise 15.5.

SAMPLE EXERCISE 15.5



The pH of a Buffered Solution III

A buffered solution contains 0.25 M NH_3 ($K_b = 1.8 \times 10^{-5}$) and $0.40 \text{ M NH}_4\text{Cl}$. Calculate the pH of this solution.

SOLUTION

The major species in solution are



From the dissolved NH_4Cl

Since Cl^- is such a weak base and water is a weak acid or base, the important equilibrium is



and

$$K_b = 1.8 \times 10^{-5} = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

The appropriate ICE table is:

	$\text{NH}_3(aq)$	+	$\text{H}_2\text{O}(l)$	$\rightleftharpoons$	$\text{NH}_4^+(aq)$	+	$\text{OH}^-(aq)$
Initial:	0.25		—		0.40		≈ 0
Change:	$-x$		—		$+x$		$+x$
Equilibrium:	$0.25 - x$		—		$0.40 + x$		x

Then

$$K_b = 1.8 \times 10^{-5} = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{(0.40 + x)(x)}{0.25 - x} \approx \frac{(0.40)(x)}{0.25}$$

and

$$x \approx 1.1 \times 10^{-5}$$

The approximations are valid (by the 5% rule), so

$$[\text{OH}^-] = x = 1.1 \times 10^{-5}$$

$$\text{pOH} = 4.95$$

$$\text{pH} = 14.00 - 4.95 = 9.05$$

This case is typical of a buffered solution in that the initial and equilibrium concentrations of buffering materials are essentially the same.

Alternative Solution

There is another way of looking at this problem. Since the solution contains relatively large quantities of *both* NH_4^+ and NH_3 , we can use the equilibrium



to calculate $[\text{OH}^-]$ and then calculate $[\text{H}^+]$ from K_w as we have just done. Or we can use the dissociation equilibrium for NH_4^+ , that is,



to calculate $[\text{H}^+]$ directly. *Either choice will give the same answer*, since the same equilibrium concentrations of NH_3 and NH_4^+ must satisfy both equilibria.

We can obtain the K_a value for NH_4^+ from the given K_b value for NH_3 , since $K_a \times K_b = K_w$:

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

Then, using the Henderson–Hasselbalch equation, we have

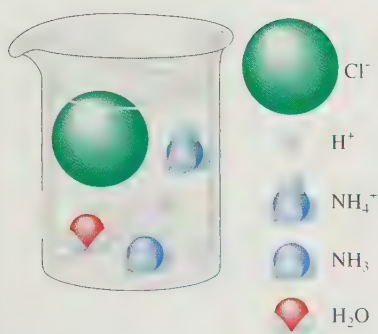
$$\begin{aligned} \text{pH} &= \text{p}K_a + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right) \\ &= 9.25 + \log\left(\frac{0.25 \text{ M}}{0.40 \text{ M}}\right) = 9.25 - 0.20 = 9.05 \end{aligned}$$

See Exercises 15.37 and 15.38.

SAMPLE EXERCISE 15.6

Adding Strong Acid to a Buffered Solution I

Calculate the pH of the solution that results when 0.10 mol gaseous HCl is added to 1.0 L of the buffered solution from Sample Exercise 15.5.

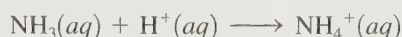


SOLUTION

Before any reaction occurs, the solution contains the following major species:



What reaction can occur? We know that H^+ will not react with Cl^- to form HCl . In contrast to Cl^- , the NH_3 molecule has a great affinity for protons (this is demonstrated by the fact that NH_4^+ is such a weak acid [$K_a = 5.6 \times 10^{-10}$]). Thus NH_3 will react with H^+ to form NH_4^+ :



Since this reaction can be assumed to go essentially to completion to form the very weak acid NH_4^+ , we will do the stoichiometry calculations before we consider the equilibrium calculations. That is, we will let the reaction run to completion and then consider the equilibrium.

The stoichiometry calculations for this process are shown below.

	NH_3	+	H^+	$\longrightarrow$	NH_4^+
Before reaction:	(1.0 L)(0.25 M) = 0.25 mol		0.10 mol ↑ Limiting reactant		(1.0 L)(0.40 M) = 0.40 mol
After reaction:	0.25 - 0.10 = 0.15 mol		0		0.40 + 0.10 = 0.50 mol

After the reaction goes to completion, the solution contains the major species



and

$$[\text{NH}_3]_0 = \frac{0.15 \text{ mol}}{1.0 \text{ L}} = 0.15 \text{ M}$$

$$[\text{NH}_4^+]_0 = \frac{0.50 \text{ mol}}{1.0 \text{ L}} = 0.50 \text{ M}$$

We can use the Henderson–Hasselbalch equation, where

$$[\text{Base}] = [\text{NH}_3] \approx [\text{NH}_3]_0 = 0.15 \text{ M}$$

$$[\text{Acid}] = [\text{NH}_4^+] \approx [\text{NH}_4^+]_0 = 0.50 \text{ M}$$

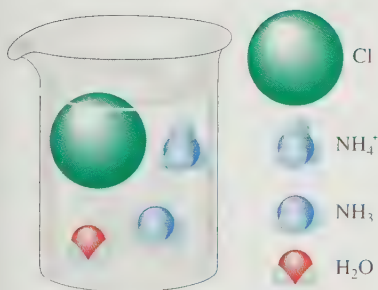
Then

$$\begin{aligned} \text{pH} &= \text{p}K_a + \log\left(\frac{[\text{NH}_3]}{[\text{NH}_4^+]}\right) \\ &= 9.25 + \log\left(\frac{0.15 \text{ M}}{0.50 \text{ M}}\right) = 9.25 - 0.52 = 8.73 \end{aligned}$$

Note that the addition of HCl only slightly decreases the pH, as we would expect in a buffered solution.

See Exercise 15.39.

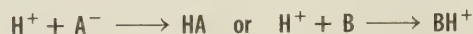
Remember: Think about the chemistry first. Ask yourself if a reaction will occur among the major species.



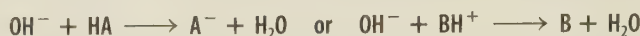
Summary of the Most Important Characteristics of Buffered Solutions

■ Buffered solutions contain relatively large concentrations of a weak acid and the corresponding weak base. They can involve a weak acid HA and the conjugate base A^- or a weak base B and the conjugate acid BH^+ .

■ When H^+ is added to a buffered solution, it reacts essentially to completion with the weak base present:



■ When OH^- is added to a buffered solution, it reacts essentially to completion with the weak acid present:



■ The pH in the buffered solution is determined by the ratio of the concentrations of the weak acid and weak base. As long as this ratio remains virtually constant, the pH will remain virtually constant. This will be the case as long as the concentrations of the buffering materials (HA and A^- or B and BH^+) are large compared with the amounts of H^+ or OH^- added.

15.3 Buffering Capacity

A buffer with a large capacity contains large concentrations of the buffering components.

The **buffering capacity** of a buffered solution represents the amount of protons or hydroxide ions the buffer can absorb without a significant change in pH. A buffer with a large capacity contains large concentrations of buffering components and so can absorb a relatively large amount of protons or hydroxide ions and show little pH change. *The pH of a buffered solution is determined by the ratio $[A^-]/[HA]$. The capacity of a buffered solution is determined by the magnitudes of $[HA]$ and $[A^-]$.*

SAMPLE EXERCISE 15.7

Adding Strong Acid to a Buffered Solution II

Calculate the change in pH that occurs when 0.010 mol gaseous HCl is added to 1.0 L of each of the following solutions:

Solution A: 5.00 M $HC_2H_3O_2$ and 5.00 M $NaC_2H_3O_2$

Solution B: 0.050 M $HC_2H_3O_2$ and 0.050 M $NaC_2H_3O_2$

For acetic acid, $K_a = 1.8 \times 10^{-5}$.

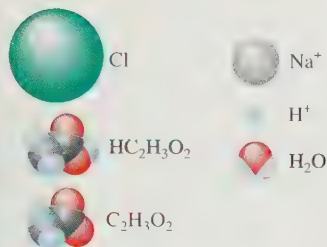
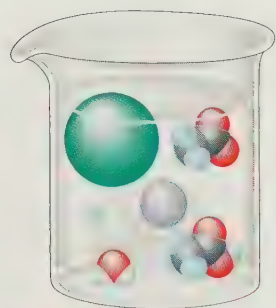
SOLUTION

For both solutions the initial pH can be determined from the Henderson–Hasselbalch equation:

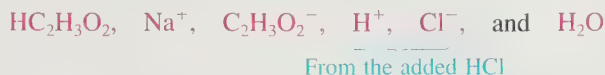
$$pH = pK_a + \log\left(\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]}\right)$$

In each case, $[C_2H_3O_2^-] = [HC_2H_3O_2]$. Therefore, the initial pH for both A and B is

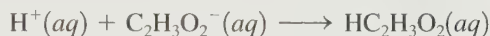
$$pH = pK_a + \log(1) = pK_a = -\log(1.8 \times 10^{-5}) = 4.74$$



After the addition of HCl to each of these solutions, the major species *before any reaction occurs* are



Will any reactions occur among these species? Note that we have a relatively large quantity of H^+ , which will readily react with any effective base. We know that Cl^- will not react with H^+ to form HCl in water. However, $\text{C}_2\text{H}_3\text{O}_2^-$ will react with H^+ to form the weak acid $\text{HC}_2\text{H}_3\text{O}_2$:



Because $\text{HC}_2\text{H}_3\text{O}_2$ is a weak acid, we assume that this reaction runs to completion; the 0.010 mol of added H^+ will convert 0.010 mol $\text{C}_2\text{H}_3\text{O}_2^-$ to 0.010 mol $\text{HC}_2\text{H}_3\text{O}_2$.

For solution A (since the solution volume is 1.0 L, the number of moles equals the molarity), the following calculations apply:

	H^+	+	$\text{C}_2\text{H}_3\text{O}_2^-$	$\longrightarrow$	$\text{HC}_2\text{H}_3\text{O}_2$
Before reaction:	0.010 M		5.00 M		5.00 M
After reaction:	0		4.99 M		5.01 M

The new pH can be obtained by substituting the new concentrations into the Henderson–Hasselbalch equation:

$$\begin{aligned} \text{pH} &= \text{p}K_a + \log\left(\frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]}\right) \\ &= 4.74 + \log\left(\frac{4.99}{5.01}\right) = 4.74 - 0.0017 = 4.74 \end{aligned}$$

There is virtually no change in pH for solution A when 0.010 mol gaseous HCl is added.

For solution B, the following calculations apply:

	H^+	+	$\text{C}_2\text{H}_3\text{O}_2^-$	$\longrightarrow$	$\text{HC}_2\text{H}_3\text{O}_2$
Before reaction:	0.010 M		0.050 M		0.050 M
After reaction:	0		0.040 M		0.060 M

The new pH is

$$\begin{aligned} \text{pH} &= 4.74 + \log\left(\frac{0.040}{0.060}\right) \\ &= 4.74 - 0.18 = 4.56 \end{aligned}$$

Although the pH change for solution B is small, a change did occur, which is in contrast to solution A.

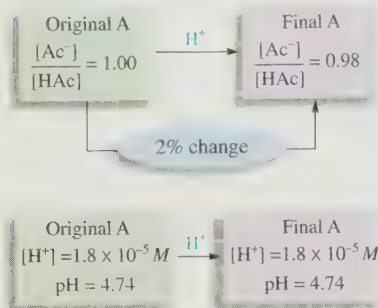
These results show that solution A, which contains much larger quantities of buffering components, has a much higher buffering capacity than solution B.

See Exercises 15.39 and 15.40.

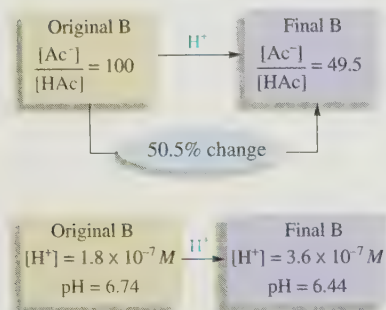
Original solution		New solution
$\frac{[\text{A}^-]}{[\text{HA}]} = \frac{5.00}{5.00} = 1.00$	$\xrightarrow[\text{added}]{\text{H}^+}$	$\frac{[\text{A}^-]}{[\text{HA}]} = \frac{4.99}{5.01} = 0.996$

Original solution		New solution
$\frac{[\text{A}^-]}{[\text{HA}]} = \frac{0.050}{0.050} = 1.0$	$\xrightarrow[\text{added}]{\text{H}^+}$	$\frac{[\text{A}^-]}{[\text{HA}]} = \frac{0.040}{0.060} = 0.67$

Solution A



Solution B

**TABLE 15.1** Change in $[\text{C}_2\text{H}_3\text{O}_2^-]/[\text{HC}_2\text{H}_3\text{O}_2]$ for Two Solutions When 0.01 mol H^+ Is Added to 1.0 L of Each

Solution	$\left(\frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]}\right)_{\text{orig}}$	$\left(\frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]}\right)_{\text{new}}$	Change	Percent Change
A	$\frac{1.00 M}{1.00 M} = 1.00$	$\frac{0.99 M}{1.01 M} = 0.98$	$1.00 \rightarrow 0.98$	2.00%
B	$\frac{1.00 M}{0.01 M} = 100$	$\frac{0.99 M}{0.02 M} = 49.5$	$100 \rightarrow 49.5$	50.5%

We have seen that the pH of a buffered solution depends on the ratio of the concentrations of buffering components. When this ratio is least affected by added protons or hydroxide ions, the solution is the most resistant to a change in pH. To find the ratio that gives optimal buffering, let's suppose we have a buffered solution containing a large concentration of acetate ion and only a small concentration of acetic acid. Addition of protons to form acetic acid will produce a relatively large *percent* change in the concentration of acetic acid and so will produce a relatively large change in the ratio $[\text{C}_2\text{H}_3\text{O}_2^-]/[\text{HC}_2\text{H}_3\text{O}_2]$ (see Table 15.1). Similarly, if hydroxide ions are added to remove some acetic acid, the percent change in the concentration of acetic acid is again large. The same effects are seen if the initial concentration of acetic acid is large and that of acetate ion is small.

Because large changes in the ratio $[\text{A}^-]/[\text{HA}]$ will produce large changes in pH, we want to avoid this situation for the most effective buffering. This type of reasoning leads us to the general conclusion that optimal buffering occurs when $[\text{HA}]$ is equal to $[\text{A}^-]$. It is for this condition that the ratio $[\text{A}^-]/[\text{HA}]$ is most resistant to change when H^+ or OH^- is added to the buffered solution. This means that when choosing the buffering components for a specific application, we want $[\text{A}^-]/[\text{HA}]$ to equal 1. It follows that since

$$\text{pH} = \text{p}K_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right) = \text{p}K_a + \log(1) = \text{p}K_a$$

the $\text{p}K_a$ of the weak acid to be used in the buffer should be as close as possible to the desired pH. For example, suppose we need a buffered solution with a pH of 4.00. The most effective buffering will occur when $[\text{HA}]$ is equal to $[\text{A}^-]$. From the Henderson–Hasselbalch equation,

$$\text{pH} = \text{p}K_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$$

$\uparrow$ 4.00 is wanted $\uparrow$ Ratio = 1 for most effective buffer

That is, $4.00 = \text{p}K_a + \log(1) = \text{p}K_a + 0$ and $\text{p}K_a = 4.00$

Thus the best choice of a weak acid is one that has $\text{p}K_a = 4.00$ or $K_a = 1.0 \times 10^{-4}$.

SAMPLE EXERCISE 15.8

Preparing a Buffer

A chemist needs a solution buffered at pH 4.30 and can choose from the following acids (and their sodium salts):

- a. chloroacetic acid ($K_a = 1.35 \times 10^{-3}$)
- b. propanoic acid ($K_a = 1.3 \times 10^{-5}$)
- c. benzoic acid ($K_a = 6.4 \times 10^{-5}$)
- d. hypochlorous acid ($K_a = 3.5 \times 10^{-8}$)

Calculate the ratio $[HA]/[A^-]$ required for each system to yield a pH of 4.30. Which system will work best?

SOLUTION

A pH of 4.30 corresponds to

$$[H^+] = 10^{-4.30} = \text{antilog}(-4.30) = 5.0 \times 10^{-5} M$$

Since K_a values rather than pK_a values are given for the various acids, we use Equation (15.1)

$$[H^+] = K_a \frac{[HA]}{[A^-]}$$

rather than the Henderson–Hasselbalch equation. We substitute the required $[H^+]$ and K_a for each acid into Equation (15.1) to calculate the ratio $[HA]/[A^-]$ needed in each case.

Acid	$[H^+] = K_a \frac{[HA]}{[A^-]}$	$\frac{[HA]}{[A^-]}$
a. Chloroacetic	$5.0 \times 10^{-5} = 1.35 \times 10^{-3} \left(\frac{[HA]}{[A^-]} \right)$	3.7×10^{-2}
b. Propanoic	$5.0 \times 10^{-5} = 1.3 \times 10^{-5} \left(\frac{[HA]}{[A^-]} \right)$	3.8
c. Benzoic	$5.0 \times 10^{-5} = 6.4 \times 10^{-5} \left(\frac{[HA]}{[A^-]} \right)$	0.78
d. Hypochlorous	$5.0 \times 10^{-5} = 3.5 \times 10^{-8} \left(\frac{[HA]}{[A^-]} \right)$	1.4×10^3

Since $[HA]/[A^-]$ for benzoic acid is closest to 1, the system of benzoic acid and its sodium salt will be the best choice among those given for buffering a solution at pH 4.3. This example demonstrates the principle that the optimal buffering system has a pK_a value close to the desired pH. The pK_a for benzoic acid is 4.19.

See Exercises 15.45 and 15.46.

15.4 Titrations and pH Curves

As we saw in Chapter 4, a titration is commonly used to determine the amount of acid or base in a solution. This process involves a solution of known concentration (the titrant) delivered from a buret into the unknown solution until the substance being analyzed is just consumed. The stoichiometric (equivalence) point is often signaled by the color change of an indicator. In this section we will discuss the pH changes that occur during an acid–base titration. We will use this information later to show how an appropriate indicator can be chosen for a particular titration.



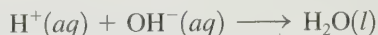
A setup used to do the pH titration of an acid or a base.

$$\begin{aligned}
 1 \text{ millimole} &= 1 \times 10^{-3} \text{ mol} \\
 1 \text{ mL} &= 1 \times 10^{-3} \text{ L} \\
 \frac{\text{mmol}}{\text{mL}} &= \frac{\text{mol}}{\text{L}} = M
 \end{aligned}$$

The progress of an acid–base titration is often monitored by plotting the pH of the solution being analyzed as a function of the amount of titrant added. Such a plot is called a **pH curve** or **titration curve**.

Strong Acid–Strong Base Titrations

The net ionic reaction for a strong acid–strong base titration is



To compute $[\text{H}^+]$ at a given point in the titration, we must determine the amount of H^+ that remains at that point and divide by the total volume of the solution. Before we proceed, we need to consider a new unit, which is especially convenient for titrations. Since titrations usually involve small quantities (burets are typically graduated in milliliters), the mole is inconveniently large. Therefore, we will use the **millimole** (abbreviated **mmol**), which, as the prefix indicates, is a thousandth of a mole:

$$1 \text{ mmol} = \frac{1 \text{ mol}}{1000} = 10^{-3} \text{ mol}$$

So far we have defined molarity only in terms of moles per liter. We can now define it in terms of *millimoles per milliliter*, as shown below:

$$\text{Molarity} = \frac{\text{mol solute}}{\text{L solution}} = \frac{\frac{\text{mol solute}}{1000}}{\frac{\text{L solution}}{1000}} = \frac{\text{mmol solute}}{\text{mL solution}}$$

A 1.0 *M* solution thus contains 1.0 mole of solute per liter of solution or, *equivalently*, 1.0 millimole of solute per milliliter of solution. Just as we obtain the number of moles of solute from the product of the volume in liters and the molarity, we obtain the number of millimoles of solute from the product of the volume in milliliters and the molarity:

$$\text{Number of mmol} = \text{volume (in mL)} \times \text{molarity}$$

CASE STUDY: Strong Acid–Strong Base Titration

We will illustrate the calculations involved in a strong acid–strong base titration by considering the titration of 50.0 mL of 0.200 *M* HNO_3 with 0.100 *M* NaOH . We will calculate the pH of the solution at selected points during the course of the titration, where specific volumes of 0.100 *M* NaOH have been added.

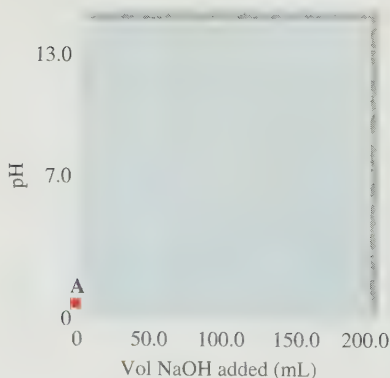
A. No NaOH has been added.

Since HNO_3 is a strong acid (is completely dissociated), the solution contains the major species



and the pH is determined by the H^+ from the nitric acid. Since 0.200 *M* HNO_3 contains 0.200 *M* H^+ ,

$$[\text{H}^+] = 0.200 \text{ M} \quad \text{and} \quad \text{pH} = 0.699$$



B. 10.0 mL of 0.100 M NaOH has been added.

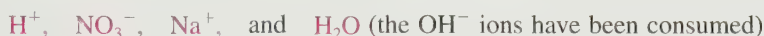
In the mixed solution *before any reaction occurs*, the major species are



Note that large quantities of both H^+ and OH^- are present. The 1.00 mmol ($10.0 \text{ mL} \times 0.100 \text{ M}$) of added OH^- will react with 1.00 mmol H^+ to form water:

	H^+	+	OH^-	$\longrightarrow$	H_2O
Before	$50.0 \text{ mL} \times 0.200 \text{ M}$		$10.0 \text{ mL} \times 0.100 \text{ M}$		
reaction:	$= 10.0 \text{ mmol}$		$= 1.00 \text{ mmol}$		
After	$10.0 - 1.00$		$1.00 - 1.00$		
reaction:	$= 9.0 \text{ mmol}$		$= 0$		

After the reaction, the solution contains



and the pH will be determined by the H^+ remaining:

$$[\text{H}^+] = \frac{\text{mmol H}^+ \text{ left}}{\text{volume of solution (mL)}} = \frac{9.0 \text{ mmol}}{\underbrace{(50.0 + 10.0) \text{ mL}}_{\substack{\text{Original volume of} \\ \text{HNO}_3 \text{ solution} \quad \quad \quad \text{Volume of} \\ \quad \quad \quad \text{NaOH added}}}} = 0.15 \text{ M}$$

$$\text{pH} = -\log(0.15) = 0.82$$

C. 20.0 mL (total) of 0.100 M NaOH has been added.

We consider this point from the perspective that a total of 20.0 mL NaOH has been added to the *original* solution, rather than that 10.0 mL has been added to the solution from point B. It is best to go back to the original solution each time so that a mistake made at an earlier point does not show up in each succeeding calculation. As before, the added OH^- will react with H^+ to form water:

	H^+	+	OH^-	$\longrightarrow$	H_2O
Before	$50.0 \text{ mL} \times 0.200 \text{ M}$		$20.0 \text{ mL} \times 0.100 \text{ M}$		
reaction:	$= 10.0 \text{ mmol}$		$= 2.00 \text{ mmol}$		
After	$10.0 - 2.00$		$2.00 - 2.00$		
reaction:	$= 8.00 \text{ mmol}$		$= 0 \text{ mmol}$		

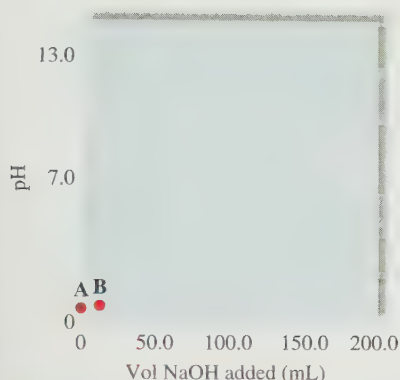
After the reaction

$$[\text{H}^+] = \frac{\overset{\text{(H}^+ \text{ remaining)}}{8.00 \text{ mmol}}}{(50.0 + 20.0) \text{ mL}} = 0.11 \text{ M}$$

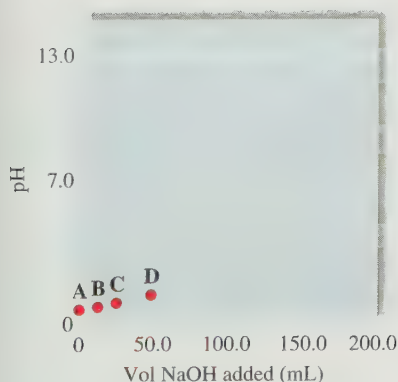
$$\text{pH} = 0.942$$

D. 50.0 mL (total) of 0.100 M NaOH has been added.

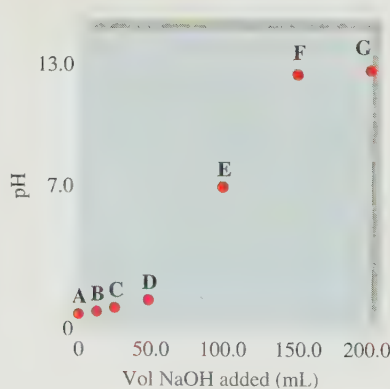
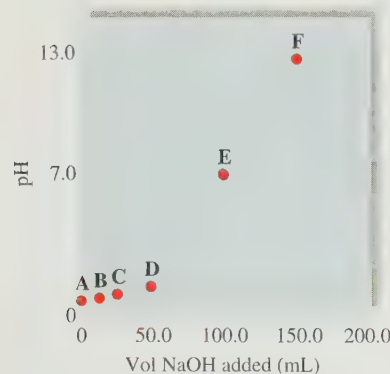
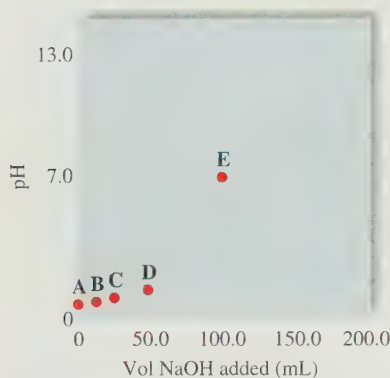
Proceeding exactly as for points B and C, the pH is found to be 1.301.



The final solution volume is the sum of the original volume of HNO_3 and the volume of added NaOH.



Equivalence (stoichiometric) point: The point in the titration where an amount of base has been added to exactly react with all the acid originally present.



E. 100.0 mL (total) of 0.100 M NaOH has been added.

At this point the amount of NaOH that has been added is

$$100.0 \text{ mL} \times 0.100 \text{ M} = 10.0 \text{ mmol}$$

The original amount of nitric acid was

$$50.0 \text{ mL} \times 0.200 \text{ M} = 10.0 \text{ mmol}$$

Enough OH^- has been added to react exactly with the H^+ from the nitric acid. This is the **stoichiometric point**, or **equivalence point**, of the titration. At this point the major species in solution are



Since Na^+ has no acid or base properties and NO_3^- is the anion of the strong acid HNO_3 and is therefore a very weak base, neither NO_3^- nor Na^+ affects the pH, and the solution is neutral (the pH is 7.00).

F. 150.0 mL (total) of 0.100 M NaOH has been added.

The stoichiometric calculations for the titration reaction are as follows:

	H^+	+	OH^-	$\longrightarrow$	H_2O
Before	50.0 mL $\times$ 0.200 M		150.0 mL $\times$ 0.100 M		
reaction:	= 10.0 mmol		= 15.0 mmol		
After	10.0 – 10.0		15.0 – 10.0		
reaction:	= 0 mmol		= 5.0 mmol		
			↑		
			Excess OH^- added		

Now OH^- is *in excess* and will determine the pH:

$$[\text{OH}^-] = \frac{\text{mmol OH}^- \text{ in excess}}{\text{volume (mL)}} = \frac{5.0 \text{ mmol}}{(50.0 + 150.0) \text{ mL}} = \frac{5.0 \text{ mmol}}{200.0 \text{ mL}} = 0.025 \text{ M}$$

Since $[\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-14}$,

$$[\text{H}^+] = \frac{1.0 \times 10^{-14}}{2.5 \times 10^{-2}} = 4.0 \times 10^{-13} \text{ M} \quad \text{and} \quad \text{pH} = 12.40$$

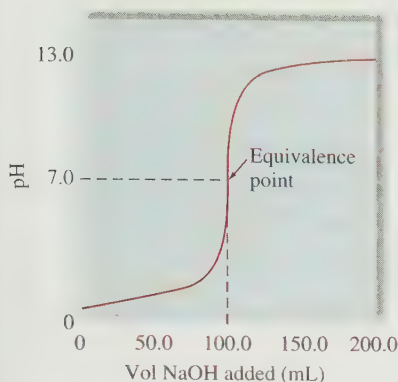
G. 200.0 mL (total) of 0.100 M NaOH has been added.

Proceeding as for point F, the pH is found to be 12.60.

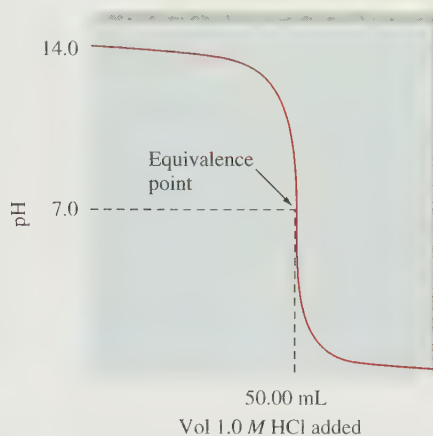
The results of these calculations are summarized by the pH curve shown in Fig. 15.1. Note that the pH changes very gradually until the titration is close to the equivalence point, where a dramatic change occurs. This behavior is due to the fact that early in the titration there is a relatively large amount of H^+ in the solution, and the addition of a given amount of OH^- thus produces a small change in pH. However, near the equivalence point $[\text{H}^+]$ is relatively small, and the addition of a small amount of OH^- produces a large change.

The pH curve in Fig. 15.1, typical of the titration of a strong acid with a strong base, has the following characteristics:

Before the equivalence point, $[\text{H}^+]$ (and hence the pH) can be calculated by dividing the number of millimoles of H^+ remaining by the total volume of the solution in millimeters.

**FIGURE 15.1**

The pH curve for the titration of 50.0 mL of 0.200 M HNO_3 with 0.100 M NaOH . Note that the equivalence point occurs at 100.0 mL of NaOH added, the point where exactly enough OH^- has been added to react with all the H^+ originally present. The pH of 7 at the equivalence point is characteristic of a strong acid–strong base titration.

**FIGURE 15.2**

The pH curve for the titration of 100.0 mL of 0.50 M NaOH with 1.0 M HCl . The equivalence point occurs at 50.00 mL of HCl added, since at this point 5.0 mmol H^+ has been added to react with the original 5.0 mmol OH^- .

At the equivalence point, the pH is 7.00.

After the equivalence point, $[\text{OH}^-]$ can be calculated by dividing the number of millimoles of excess OH^- by the total volume of the solution. Then $[\text{H}^+]$ is obtained from K_w .

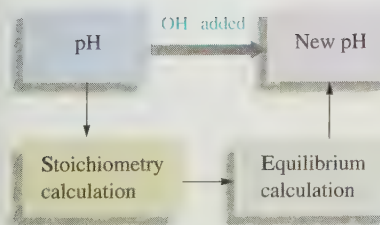
The titration of a strong base with a strong acid requires reasoning very similar to that used above, except, of course, that OH^- is in excess before the equivalence point and H^+ is in excess after the equivalence point. The pH curve for the titration of 100.0 mL of 0.50 M NaOH with 1.0 M HCl is shown in Fig. 15.2.

Titration of Weak Acids with Strong Bases

We have seen that since strong acids and strong bases are completely dissociated, the calculations to obtain the pH curves for titrations involving the two are quite straightforward. However, when the acid being titrated is a weak acid, there is a major difference: To calculate $[\text{H}^+]$ after a certain amount of strong base has been added, we must deal with the weak acid dissociation equilibrium. We have dealt with this same situation earlier in this chapter when we treated buffered solutions. Calculation of the pH curve for a titration of a weak acid with a strong base really amounts to a series of buffer problems. In performing these calculations it is very important to remember that even though the acid is weak, it *reacts essentially to completion* with hydroxide ion, a very strong base.

Calculating the pH curve for a weak acid–strong base titration involves a two-step procedure.

- ➡ **1 A stoichiometry problem.** The reaction of hydroxide ion with the weak acid is assumed to run to completion, and the concentrations of the acid *remaining* and the conjugate base *formed* are determined.
- ➡ **2 An equilibrium problem.** The position of the weak acid equilibrium is determined, and the pH is calculated.



Treat the stoichiometry and equilibrium problems separately.

It is *essential* to do these steps *separately*. Note that the procedures necessary to do these calculations have all been used before.

CASE STUDY: Weak Acid–Strong Base Titration

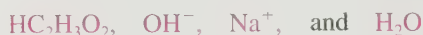
As an illustration, we will consider the titration of 50.0 mL of 0.10 *M* acetic acid ($\text{HC}_2\text{H}_3\text{O}_2$, $K_a = 1.8 \times 10^{-5}$) with 0.10 *M* NaOH. As before, we will calculate the pH at various points representing volumes of added NaOH.

A. No NaOH has been added.

This is a typical weak acid calculation of the type introduced in Chapter 14. The pH is 2.87. (Check this yourself.)

B. 10.0 mL of 0.10 *M* NaOH has been added.

The major species in the mixed solution *before any reaction takes place* are



The strong base OH^- will react with the strongest proton donor, which in this case is $\text{HC}_2\text{H}_3\text{O}_2$.

The Stoichiometry Problem

You are again doing exactly the same type of calculation already considered in Chapter 14.

	OH^-	+	$\text{HC}_2\text{H}_3\text{O}_2$	$\longrightarrow$	$\text{C}_2\text{H}_3\text{O}_2^-$	+	H_2O
Before	10 mL $\times$ 0.10 <i>M</i>		50.0 mL $\times$ 0.10 <i>M</i>		0 mmol		
reaction:	= 1.0 mmol		= 5.0 mmol				
After	1.0 – 1.0		5.0 – 1.0		1.0 mmol		
reaction:	= 0 mmol		= 4.0 mmol		$\uparrow$		
	$\uparrow$				Formed by		
	Limiting reactant				the reaction		

The Equilibrium Problem We examine the major components left in the solution *after the reaction takes place* to decide on the dominant equilibrium. The major species are



Since $\text{HC}_2\text{H}_3\text{O}_2$ is a much stronger acid than H_2O , and since $\text{C}_2\text{H}_3\text{O}_2^-$ is the conjugate base of $\text{HC}_2\text{H}_3\text{O}_2$, the pH will be determined by the position of the acetic acid dissociation equilibrium:



where

$$K_a = \frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]}$$

We follow the usual steps to complete the equilibrium calculations:

The initial concentrations are defined after the reaction with OH^- has gone to completion but before any dissociation of $\text{HC}_2\text{H}_3\text{O}_2$ occurs.

Initial Concentration		Equilibrium Concentration
$[\text{HC}_2\text{H}_3\text{O}_2]_0 = \frac{4.0 \text{ mmol}}{(50.0 + 10.0) \text{ mL}} = \frac{4.0}{60.0}$	$\xrightarrow[\text{dissociates}]{\substack{x \text{ mmol/mL} \\ \text{HC}_2\text{H}_3\text{O}_2}}$	$[\text{HC}_2\text{H}_3\text{O}_2] = \frac{4.0}{60.0} - x$
$[\text{C}_2\text{H}_3\text{O}_2^-]_0 = \frac{1.0 \text{ mmol}}{(50.0 + 10.0) \text{ mL}} = \frac{1.0}{60.0}$		$[\text{C}_2\text{H}_3\text{O}_2^-] = \frac{1.0}{60.0} + x$
$[\text{H}^+]_0 \approx 0$		$[\text{H}^+] = x$

The appropriate ICE table is:

	$\text{HC}_2\text{H}_3\text{O}_2(aq)$	$\rightleftharpoons$	$\text{H}^+(aq)$	+	$\text{C}_2\text{H}_3\text{O}_2^-(aq)$
Initial:	$\frac{4.0}{60.0}$		≈ 0		$\frac{1.0}{60.0}$
Change:	$-x$		$+x$		$+x$
Equilibrium:	$\frac{4.0}{60.0} - x$		x		$\frac{1.0}{60.0} + x$

Therefore,

$$1.8 \times 10^{-5} = K_a = \frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = \frac{x\left(\frac{1.0}{60.0} + x\right)}{\frac{4.0}{60.0} - x} \approx \frac{x\left(\frac{1.0}{60.0}\right)}{\frac{4.0}{60.0}} = \left(\frac{1.0}{4.0}\right)x$$

$$x = \left(\frac{4.0}{1.0}\right)(1.8 \times 10^{-5}) = 7.2 \times 10^{-5} = [\text{H}^+] \quad \text{and} \quad \text{pH} = 4.14$$

Note that the approximations made are well within the 5% rule.

C. 25.0 mL (total) of 0.10 M NaOH has been added.

The procedure here is very similar to that used at point B and will only be summarized briefly. The stoichiometry problem is summarized as follows:

	OH^-	+	$\text{HC}_2\text{H}_3\text{O}_2$	$\longrightarrow$	$\text{C}_2\text{H}_3\text{O}_2^-$	+	H_2O
Before reaction:	$25.0 \text{ mL} \times 0.10 \text{ M}$ $= 2.5 \text{ mmol}$		$50.0 \text{ mL} \times 0.10 \text{ M}$ $= 5.0 \text{ mmol}$		0 mmol		
After reaction:	$2.5 - 2.5 = 0$		$5.0 - 2.5$ $= 2.5 \text{ mmol}$		2.5 mmol		

After the reaction, the major species in solution are



The equilibrium that will control the pH is



and the pertinent concentrations are as follows:

Initial Concentration		Equilibrium Concentration
$[\text{HC}_2\text{H}_3\text{O}_2]_0 = \frac{2.5 \text{ mmol}}{(50.0 + 25.0) \text{ mL}}$	$\xrightarrow[\text{dissociates}]{\substack{x \text{ mmol/mL} \\ \text{HC}_2\text{H}_3\text{O}_2}}$	$[\text{HC}_2\text{H}_3\text{O}_2] = \frac{2.5}{75.0} - x$
$[\text{C}_2\text{H}_3\text{O}_2^-]_0 = \frac{2.5 \text{ mmol}}{(50.0 + 25.0) \text{ mL}}$		$[\text{C}_2\text{H}_3\text{O}_2^-] = \frac{2.5}{75.0} + x$
$[\text{H}^+]_0 \approx 0$		$[\text{H}^+] = x$

The corresponding ICE table is:

	$\text{HC}_2\text{H}_3\text{O}_2(aq)$	$\rightleftharpoons$	$\text{H}^+(aq)$	+	$\text{C}_2\text{H}_3\text{O}_2^-(aq)$
Initial:	$\frac{2.5}{75.0}$		≈ 0		$\frac{2.5}{75.0}$
Change:	$-x$		$+x$		$+x$
Equilibrium:	$\frac{2.5}{75.0} - x$		x		$\frac{2.5}{75.0} + x$

Therefore,

$$1.8 \times 10^{-5} = K_a = \frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = \frac{x\left(\frac{2.5}{75.0} + x\right)}{\frac{2.5}{75.0} - x} \approx \frac{x\left(\frac{2.5}{75.0}\right)}{\frac{2.5}{75.0}}$$

$$x = 1.8 \times 10^{-5} = [\text{H}^+] \quad \text{and} \quad \text{pH} = 4.74$$

This is a special point in the titration because it is *halfway to the equivalence point*. The original solution, 50.0 mL of 0.10 M $\text{HC}_2\text{H}_3\text{O}_2$, contained 5.0 mmol $\text{HC}_2\text{H}_3\text{O}_2$. Thus 5.0 mmol OH^- is required to reach the equivalence point. That is, 50 mL NaOH is required, since

$$(50.0 \text{ mL})(0.10 M) = 5.0 \text{ mmol}$$

After 25.0 mL NaOH has been added, half the original $\text{HC}_2\text{H}_3\text{O}_2$ has been converted to $\text{C}_2\text{H}_3\text{O}_2^-$. At this point in the titration $[\text{HC}_2\text{H}_3\text{O}_2]_0$ is equal to $[\text{C}_2\text{H}_3\text{O}_2^-]_0$. We can neglect the effect of dissociation; that is,

$$[\text{HC}_2\text{H}_3\text{O}_2] = [\text{HC}_2\text{H}_3\text{O}_2]_0 - x \approx [\text{HC}_2\text{H}_3\text{O}_2]_0$$

$$[\text{C}_2\text{H}_3\text{O}_2^-] = [\text{C}_2\text{H}_3\text{O}_2^-]_0 + x \approx [\text{C}_2\text{H}_3\text{O}_2^-]_0$$

The expression for K_a at the halfway point is

$$K_a = \frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = \frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]_0}{[\text{HC}_2\text{H}_3\text{O}_2]_0} = [\text{H}^+]$$

Equal at the
halfway point

Then, *at the halfway point* in the titration,

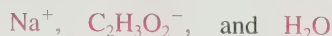
$$[\text{H}^+] = K_a \quad \text{and} \quad \text{pH} = \text{p}K_a$$

D. 40.0 mL (total) of 0.10 M NaOH has been added.

The procedures required here are the same as those used for points B and C. The pH is 5.35. (Check this yourself.)

E. 50.0 mL (total) of 0.10 M NaOH has been added.

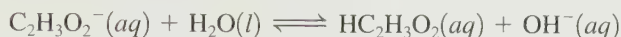
This is the equivalence point of the titration; 5.0 mmol OH^- has been added, which will just react with the 5.0 mmol $\text{HC}_2\text{H}_3\text{O}_2$ originally present. At this point the solution contains the major species



At this point, half the acid has been used up, so



Note that the solution contains $\text{C}_2\text{H}_3\text{O}_2^-$, which is a base. Remember that a base wants to combine with a proton, and the only source of protons in this solution is water. Thus the reaction will be



This is a *weak base* reaction characterized by K_b :

$$K_b = \frac{[\text{HC}_2\text{H}_3\text{O}_2][\text{OH}^-]}{[\text{C}_2\text{H}_3\text{O}_2^-]} = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

The relevant concentrations are as follows:

Initial Concentration (before any $\text{C}_2\text{H}_3\text{O}_2^-$ reacts with H_2O)		Equilibrium Concentration
$[\text{C}_2\text{H}_3\text{O}_2^-]_0 = \frac{5.0 \text{ mmol}}{(50.0 + 50.0) \text{ mL}}$		
$= 0.050 \text{ M}$	$\xrightarrow[\text{with } \text{H}_2\text{O}]{\substack{x \text{ mmol/mL} \\ \text{C}_2\text{H}_3\text{O}_2^- \text{ reacts}}}$	$[\text{C}_2\text{H}_3\text{O}_2^-] = 0.050 - x$
$[\text{OH}^-]_0 \approx 0$		$[\text{OH}^-] = x$
$[\text{HC}_2\text{H}_3\text{O}_2]_0 = 0$		$[\text{HC}_2\text{H}_3\text{O}_2] = x$

The corresponding ICE table is:

	$\text{C}_2\text{H}_3\text{O}_2^-(aq)$	+	$\text{H}_2\text{O}(l)$	$\rightleftharpoons$	$\text{HC}_2\text{H}_3\text{O}_2(aq)$	+	$\text{OH}^-(aq)$
Initial:	0.050		—		0		≈ 0
Change:	$-x$		—		$+x$		$+x$
Equilibrium:	$0.050 - x$		—		x		x

Therefore,

$$5.6 \times 10^{-10} = K_b = \frac{[\text{HC}_2\text{H}_3\text{O}_2][\text{OH}^-]}{[\text{C}_2\text{H}_3\text{O}_2^-]} = \frac{(x)(x)}{0.050 - x} \approx \frac{x^2}{0.050}$$

$$x \approx 5.3 \times 10^{-6}$$

The approximation is valid (by the 5% rule), so

$$[\text{OH}^-] = 5.3 \times 10^{-6} \text{ M}$$

and

$$[\text{H}^+][\text{OH}^-] = K_w = 1.0 \times 10^{-14}$$

$$[\text{H}^+] = 1.9 \times 10^{-9} \text{ M}$$

$$\text{pH} = 8.72$$

The pH at the equivalence point of a titration of a weak acid with a strong base is always greater than 7.

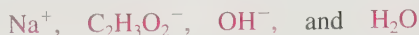
This is another important result: *The pH at the equivalence point of a titration of a weak acid with a strong base is always greater than 7.* This is so because the anion of the acid, which remains in solution at the equivalence point, is a base. In contrast, for the titration of a strong acid with a strong base, the pH at the equivalence point is 7.0, because the anion remaining in this case is *not* an effective base.

F. 60.0 mL (total) of 0.10 M NaOH has been added.

At this point, excess OH^- has been added. The stoichiometric calculations are as follows:

	OH^-	+	$\text{HC}_2\text{H}_3\text{O}_2$	$\longrightarrow$	$\text{C}_2\text{H}_3\text{O}_2^-$	+	H_2O
Before	$60.0 \text{ mL} \times 0.10 \text{ M}$		$50.0 \text{ mL} \times 0.10 \text{ M}$				
reaction:	$= 6.0 \text{ mmol}$		$= 5.0 \text{ mmol}$		0 mmol		
After	$6.0 - 5.0$						
reaction:	$= 1.0 \text{ mmol in excess}$		$5.0 - 5.0 = 0$		5.0 mmol		

After the reaction is complete, the solution contains the major species



There are two bases in this solution, OH^- and $\text{C}_2\text{H}_3\text{O}_2^-$. However, $\text{C}_2\text{H}_3\text{O}_2^-$ is a weak base compared with OH^- . Therefore, the amount of OH^- produced by reaction of $\text{C}_2\text{H}_3\text{O}_2^-$ with H_2O will be small compared with the excess OH^- already in solution. You can verify this conclusion by looking at point E, where only $5.3 \times 10^{-6} \text{ M}$ OH^- was produced by $\text{C}_2\text{H}_3\text{O}_2^-$. The amount in this case will be even smaller, since the excess OH^- will push the K_b equilibrium to the left.

Thus the pH is determined by the excess OH^- :

$$[\text{OH}^-] = \frac{\text{mmol of OH}^- \text{ in excess}}{\text{volume (in mL)}} = \frac{1.0 \text{ mmol}}{(50.0 + 60.0) \text{ mL}} \\ = 9.1 \times 10^{-3} \text{ M}$$

$$\text{and } [\text{H}^+] = \frac{1.0 \times 10^{-14}}{9.1 \times 10^{-3}} = 1.1 \times 10^{-12} \text{ M} \\ \text{pH} = 11.96$$

G. 75.0 mL (total) of 0.10 M NaOH has been added.

The procedure needed here is very similar to that for point F. The pH is 12.30. (Check this yourself.)

The pH curve for this titration is shown in Fig. 15.3. It is important to note the differences between this curve and that in Fig. 15.1. For example, the shapes of the plots are quite different before the equivalence point, although they are very similar after that point. (The shapes of the strong and weak acid curves are the same after the equivalence points because excess OH^- controls the pH in this region in both cases.) Near the beginning of the titration of the weak acid, the pH increases more rapidly than it does in the strong acid case. It levels off near the halfway point and

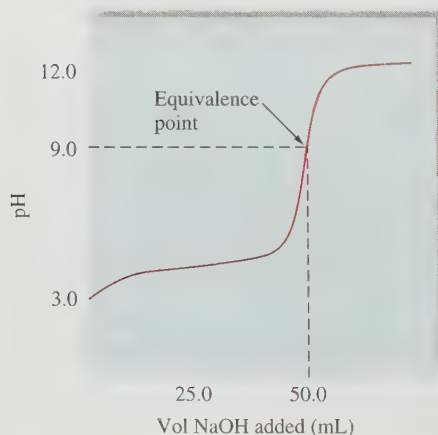
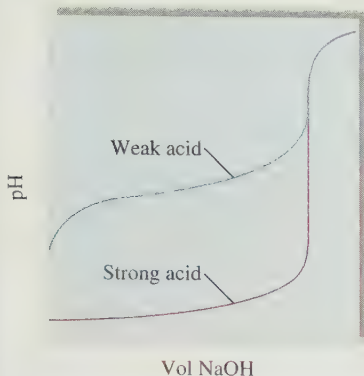


FIGURE 15.3

The pH curve for the titration of 50.0 mL of 0.100 M $\text{HC}_2\text{H}_3\text{O}_2$ with 0.100 M NaOH. Note that the equivalence point occurs at 50.0 mL of NaOH added, where the amount of added OH^- exactly equals the original amount of acid. The pH at the equivalence point is greater than 7.0 because the $\text{C}_2\text{H}_3\text{O}_2^-$ ion present at this point is a base and reacts with water to produce OH^- .



The equivalence point is defined by the stoichiometry, not by the pH.

SAMPLE EXERCISE 15.9

Titration of a Weak Acid

Hydrogen cyanide gas (HCN), a powerful respiratory inhibitor, is highly toxic. It is a very weak acid ($K_a = 6.2 \times 10^{-10}$) when dissolved in water. If a 50.0-mL sample of 0.100 M HCN is titrated with 0.100 M NaOH, calculate the pH of the solution

- after 8.00 mL of 0.100 M NaOH has been added.
- at the halfway point of the titration.
- at the equivalence point of the titration.

SOLUTION

- a. *The stoichiometry problem.* After 8.00 mL of 0.100 M NaOH has been added, the following calculations apply:

	HCN	+	OH ⁻	→	CN ⁻	+ H ₂ O
Before	50.0 mL × 0.100 M		8.00 mL × 0.100 M		0 mmol	
reaction:	= 5.00 mmol		= 0.800 mmol			
After	5.00 - 0.800					
reaction:	= 4.20 mmol		0.800 - 0.800 = 0		0.800 mmol	

The equilibrium problem. Since the solution contains the major species



the position of the acid dissociation equilibrium



will determine the pH.

Initial Concentration		Equilibrium Concentration
$[\text{HCN}]_0 = \frac{4.2 \text{ mmol}}{(50.0 + 8.0) \text{ mL}}$	$x \text{ mmol/mL}$ HCN dissociates →	$[\text{HCN}] = \frac{4.2}{58.0} - x$
$[\text{CN}^-]_0 = \frac{0.800 \text{ mmol}}{(50.0 + 8.0) \text{ mL}}$		$[\text{CN}^-] = \frac{0.80}{58.0} + x$
$[\text{H}^+]_0 \approx 0$		$[\text{H}^+] = x$

The corresponding ICE table is:

	$\text{HCN}(aq)$	$\rightleftharpoons$	$\text{H}^+(aq)$	+	$\text{CN}^-(aq)$
Initial:	$\frac{4.2}{58.0}$		≈ 0		$\frac{0.80}{58.0}$
Change:	$-x$		$+x$		$+x$
Equilibrium:	$\frac{4.2}{58.0} - x$		x		$\frac{0.80}{58.0} + x$

Substituting the equilibrium concentrations into the expression for K_a gives

$$6.2 \times 10^{-10} = K_a = \frac{[\text{H}^+][\text{CN}^-]}{[\text{HCN}]} = \frac{x \left(\frac{0.80}{58.0} + x \right)}{\frac{4.2}{58.0} - x} \approx \frac{x \left(\frac{0.80}{58.0} \right)}{\left(\frac{4.2}{58.0} \right)} = x \left(\frac{0.80}{4.2} \right)$$

$$x = 3.3 \times 10^{-9} M = [\text{H}^+] \quad \text{and} \quad \text{pH} = 8.49$$

The approximations made here are well within the 5% rule.

- b.** At the halfway point of the titration. The amount of HCN originally present can be obtained from the original volume and molarity:

$$50.0 \text{ mL} \times 0.100 M = 5.00 \text{ mmol}$$

Thus the halfway point will occur when 2.50 mmol OH^- has been added:

$$\text{Volume of NaOH (in mL)} \times 0.100 M = 2.50 \text{ mmol OH}^-$$

or

$$\text{Volume of NaOH} = 25.0 \text{ mL}$$

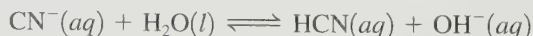
As was pointed out previously, at the halfway point $[\text{HCN}]$ is equal to $[\text{CN}^-]$ and pH is equal to $\text{p}K_a$. Thus, after 25.0 mL of 0.100 M NaOH has been added,

$$\text{pH} = \text{p}K_a = -\log(6.2 \times 10^{-10}) = 9.21$$

- c.** At the equivalence point. The equivalence point will occur when a total of 5.00 mmol OH^- has been added. Since the NaOH solution is 0.100 M, the equivalence point occurs when 50.0 mL NaOH has been added. This amount will form 5.00 mmol CN^- . The major species in solution at the equivalence point are



Thus the reaction that will control the pH involves the basic cyanide ion extracting a proton from water:



$$\text{and} \quad K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{6.2 \times 10^{-10}} = 1.6 \times 10^{-5} = \frac{[\text{HCN}][\text{OH}^-]}{[\text{CN}^-]}$$

Initial Concentration		Equilibrium Concentration
$[\text{CN}^-]_0 = \frac{5.00 \text{ mmol}}{(50.0 + 50.0) \text{ mL}} = 5.00 \times 10^{-2} M$	$x \text{ mmol/mL of } \text{CN}^- \text{ reacts with } \text{H}_2\text{O} \rightarrow$	$[\text{CN}^-] = (5.00 \times 10^{-2}) - x$
$[\text{HCN}]_0 = 0$		$[\text{HCN}] = x$
$[\text{OH}^-]_0 \approx 0$		$[\text{OH}^-] = x$

The corresponding ICE table is:

	$\text{CN}^-(aq)$	+	$\text{H}_2\text{O}(l)$	$\rightleftharpoons$	$\text{HCN}(aq)$	+	$\text{OH}^-(aq)$
Initial:	0.050		—		0		0
Change:	$-x$		—		$+x$		$+x$
Equilibrium:	$0.050 - x$		—		x		x

Substituting the equilibrium concentrations into the expression for K_b and solving in the usual way gives

$$[\text{OH}^-] = x = 8.9 \times 10^{-4}$$

Then, from K_w , we have

$$[\text{H}^+] = 1.1 \times 10^{-11} \quad \text{and} \quad \text{pH} = 10.96$$

See Exercises 15.55, 15.57, and 15.58.

The amount of acid present, not its strength, determines the equivalence point.

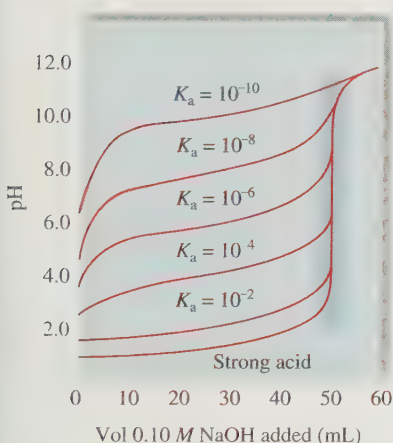


FIGURE 15.4

The pH curves for the titrations of 50.0-mL samples of 0.10 M acids with various K_a values with 0.10 M NaOH.

Two important conclusions can be drawn from a comparison of the titration of 50.0 mL of 0.1 M acetic acid covered earlier in this section and that of 50.0 mL of 0.1 M hydrocyanic acid analyzed in Sample Exercise 15.9. First, the same amount of 0.1 M NaOH is required to reach the equivalence point in both cases. The fact that HCN is a much weaker acid than $\text{HC}_2\text{H}_3\text{O}_2$ has no bearing on the amount of base required. It is the *amount* of acid, not its strength, that determines the equivalence point. Second, the pH value at the equivalence point is affected by the acid strength. For the titration of acetic acid, the pH at the equivalence point is 8.72; for the titration of hydrocyanic acid, the pH at the equivalence point is 10.96. This difference occurs because the CN^- ion is a much stronger base than the $\text{C}_2\text{H}_3\text{O}_2^-$ ion. Also, the pH at the halfway point of the titration is much higher for HCN than for $\text{HC}_2\text{H}_3\text{O}_2$, again because of the greater base strength of the CN^- ion (or equivalently, the smaller acid strength of HCN).

The strength of a weak acid has a significant effect on the shape of its pH curve. Figure 15.4 shows pH curves for 50-mL samples of 0.10 M solutions of various acids titrated with 0.10 M NaOH. Note that the equivalence point occurs in each case when the same volume of 0.10 M NaOH has been added but that the shapes of the curves are dramatically different. The weaker the acid, the greater the pH value at the equivalence point. In particular, note that the vertical region that surrounds the equivalence point becomes shorter as the acid being titrated becomes weaker. We will see in the next section that the choice of an indicator is more limited for such a titration.

Besides being used to analyze for the amount of acid or base in a solution, titrations can be used to determine the values of equilibrium constants, as shown in Sample Exercise 15.10.

Calculation of K_a

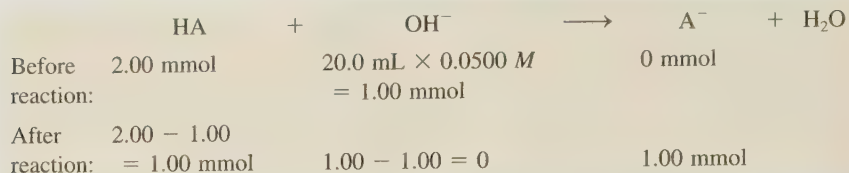
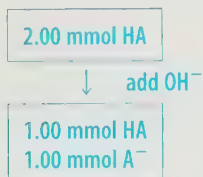
Calculating K_a

A chemist has synthesized a monoprotic weak acid and wants to determine its K_a value. To do so, the chemist dissolves 2.00 mmol of the solid acid in 100.0 mL water and titrates the resulting solution with 0.0500 M NaOH. After 20.0 mL NaOH has been added, the pH is 6.00. What is the K_a value for the acid?

SAMPLE EXERCISE 15.10

SOLUTION

The stoichiometry problem. We represent the monoprotic acid as HA. The stoichiometry for the titration reaction is shown below.



The equilibrium problem. After the reaction the solution contains the major species



The pH will be determined by the equilibrium



for which
$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

Initial Concentration		Equilibrium Concentration
$[\text{HA}]_0 = \frac{1.00 \text{ mmol}}{(100.0 + 20.0) \text{ mL}}$ $= 8.33 \times 10^{-3} M$	$\xrightarrow{x \text{ mmol/mL HA dissociates}}$	$[\text{HA}] = 8.33 \times 10^{-3} - x$
$[\text{A}^-] = \frac{1.00 \text{ mmol}}{(100.0 + 20.0) \text{ mL}}$ $= 8.33 \times 10^{-3} M$		$[\text{A}^-] = 8.33 \times 10^{-3} + x$
$[\text{H}^+]_0 \approx 0$		$[\text{H}^+] = x$

The corresponding ICE table is:

	HA(aq)	$\rightleftharpoons$	H ⁺ (aq)	+	A ⁻ (aq)
Initial:	8.33×10^{-3}		≈ 0		8.33×10^{-3}
Change:	$-x$		$+x$		$+x$
Equilibrium:	$8.33 \times 10^{-3} - x$		x		$8.33 \times 10^{-3} + x$

Note that x is known here because the pH at this point is known to be 6.00. Thus

$$x = [\text{H}^+] = \text{antilog}(-\text{pH}) = 1.0 \times 10^{-6} M$$

Substituting the equilibrium concentrations into the expression for K_a allows calculation of the K_a value:

$$\begin{aligned} K_a &= \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{x(8.33 \times 10^{-3} + x)}{(8.33 \times 10^{-3} - x)} \\ &= \frac{(1.0 \times 10^{-6})(8.33 \times 10^{-3} + 1.0 \times 10^{-6})}{(8.33 \times 10^{-3} - (1.0 \times 10^{-6}))} \\ &\approx \frac{(1.0 \times 10^{-6})(8.33 \times 10^{-3})}{8.33 \times 10^{-3}} = 1.0 \times 10^{-6} \end{aligned}$$

There is an easier way to think about this problem. The original solution contained 2.00 mmol of HA, and since 20.0 mL of added 0.0500 M NaOH contains 1.0 mmol OH^- , this is the halfway point in the titration (where $[\text{HA}]$ is equal to $[\text{A}^-]$). Thus

$$[\text{H}^+] = K_a = 1.0 \times 10^{-6}$$

See Exercise 15.63.

Titrations of Weak Bases with Strong Acids

Titrations of weak bases with strong acids can be treated using the procedures we introduced previously. As always, you should *think first about the major species in solution* and decide whether a reaction occurs that runs essentially to completion. If such a reaction does occur, let it run to completion and do the stoichiometric calculations. Finally, choose the dominant equilibrium and calculate the pH.

CASE STUDY: Weak Base–Strong Acid Titration

The calculations involved for the titration of a weak base with a strong acid will be illustrated by the titration of 100.0 mL of 0.050 M NH_3 with 0.10 M HCl.

Before the addition of any HCl.

1. Major species:



NH_3 is a base and will seek a source of protons. In this case H_2O is the only available source.

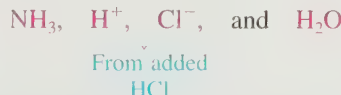
2. No reactions occur that go to completion, since NH_3 cannot readily take a proton from H_2O . This is evidenced by the small K_b value for NH_3 .
3. The equilibrium that controls the pH involves the reaction of ammonia with water:



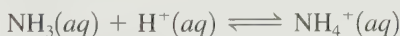
Use K_b to calculate $[\text{OH}^-]$. Although NH_3 is a weak base (compared with OH^-), it produces much more OH^- in this reaction than is produced from the autoionization of H_2O .

Before the equivalence point.

1. Major species (before any reaction occurs):



2. The NH_3 will react with H^+ from the added HCl:



This reaction proceeds essentially to completion because the NH_3 readily reacts with a free proton. This case is much different from the previous case, where H_2O was the only source of protons. The stoichiometric calculations are then carried out using the known volume of 0.10 M HCl added.

3. After the reaction of NH_3 with H^+ is run to completion, the solution contains the following major species:

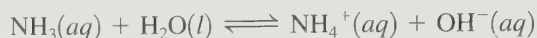


$\uparrow$
 Formed in
 titration reaction

Note that the solution contains NH_3 and NH_4^+ , and the equilibria involving these species will determine $[\text{H}^+]$. You can use either the dissociation reaction of NH_4^+



or the reaction of NH_3 with H_2O



At the equivalence point.

1. By definition, the equivalence point occurs when all the original NH_3 is converted to NH_4^+ . Thus the major species in solution are



2. No reactions occur that go to completion.
3. The dominant equilibrium (the one that controls the $[\text{H}^+]$) will be the dissociation of the weak acid NH_4^+ , for which

$$K_a = \frac{K_w}{K_b(\text{for } \text{NH}_3)}$$

Beyond the equivalence point.

1. Excess HCl has been added, and the major species are



2. No reaction occurs that goes to completion.
3. Although NH_4^+ will dissociate, it is such a weak acid that $[\text{H}^+]$ will be determined simply by the excess H^+ :

$$[\text{H}^+] = \frac{\text{mmol } \text{H}^+ \text{ in excess}}{\text{mL solution}}$$

The results of these calculations are shown in Table 15.2. The pH curve is shown in Fig. 15.5.

15.5 Acid–Base Indicators

There are two common methods for determining the equivalence point of an acid–base titration:

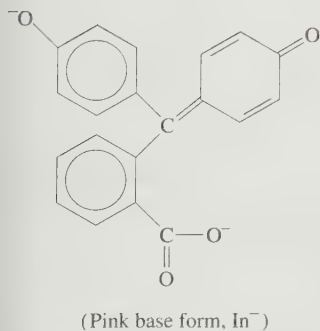
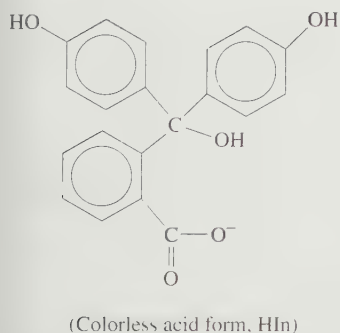
1. Use a pH meter (see Fig. 14.9) to monitor the pH and then plot the titration curve. The center of the vertical region of the pH curve indicates the equivalence point (for example, see Figs. 15.1 through 15.5).

TABLE 15.2 Summary of Results for the Titration of 100.0 mL 0.050 M NH_3 with 0.10 M HCl

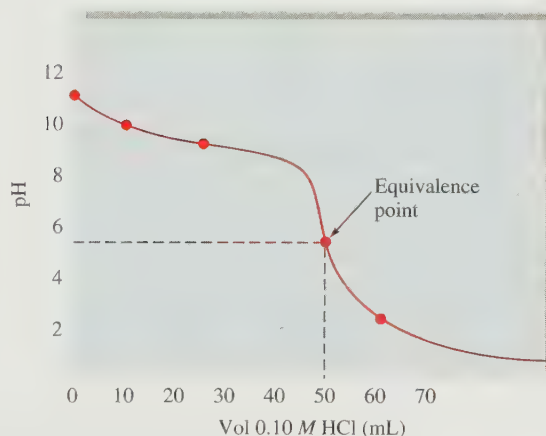
Volume of 0.10 M HCl Added (mL)	$[\text{NH}_3]_0$	$[\text{NH}_4^+]_0$	$[\text{H}^+]$	pH
0	0.05 M	0	$1.1 \times 10^{-11} \text{ M}$	10.96
10.0	$\frac{4.0 \text{ mmol}}{(100 + 10) \text{ mL}}$	$\frac{1.0 \text{ mmol}}{(100 + 10) \text{ mL}}$	$1.4 \times 10^{-10} \text{ M}$	9.85
25.0*	$\frac{2.5 \text{ mmol}}{(100 + 25) \text{ mL}}$	$\frac{2.5 \text{ mmol}}{(100 + 25) \text{ mL}}$	$5.6 \times 10^{-10} \text{ M}$	9.25
50.0†	0	$\frac{5.0 \text{ mmol}}{(100 + 50) \text{ mL}}$	$4.3 \times 10^{-6} \text{ M}$	5.36
60.0‡	0	$\frac{5.0 \text{ mmol}}{(100 + 60) \text{ mL}}$	$\frac{1.0 \text{ mmol}}{160 \text{ mL}}$ $= 6.2 \times 10^{-3} \text{ M}$	2.21

*Halfway point

†Equivalence point

‡ $[\text{H}^+]$ determined by the 1.0 mmol of excess H^+ **FIGURE 15.6**

The acid and base forms of the indicator phenolphthalein. In the acid form (HIn), the molecule is colorless. When a proton (plus H_2O) is removed to give the base form (In^-), the color changes to pink.

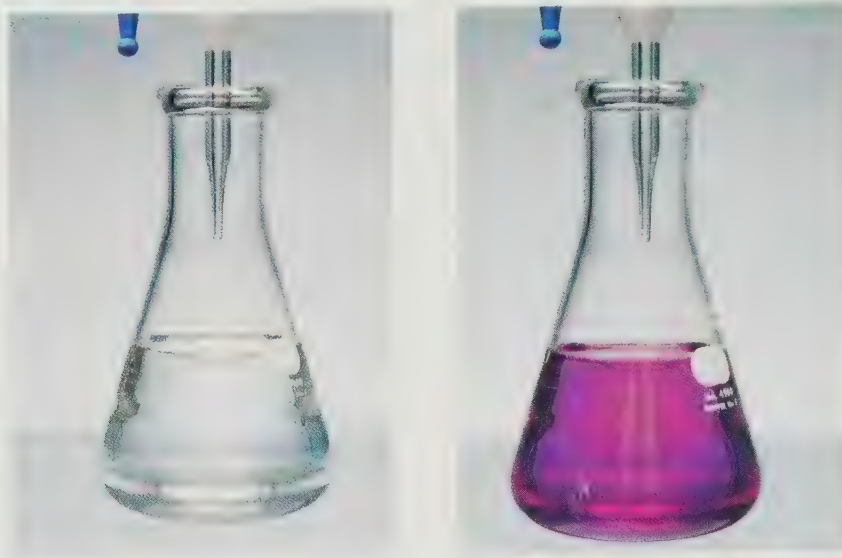
**FIGURE 15.5**

The pH curve for the titration of 100.0 mL of 0.050 M NH_3 with 0.10 M HCl. Note the pH at the equivalence point is less than 7, since the solution contains the weak acid NH_4^+ .

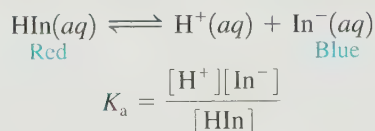
- Use an **acid-base indicator**, which marks the end point of a titration by changing color. Although the *equivalence point of a titration, defined by the stoichiometry, is not necessarily the same as the end point* (where the indicator changes color), careful selection of the indicator will ensure that the error is negligible.

The most common acid-base indicators are complex molecules that are themselves weak acids (represented by HIn). They exhibit one color when the proton is attached to the molecule and a different color when the proton is absent. For example, **phenolphthalein**, a commonly used indicator, is colorless in its HIn form and pink in its In^- , or basic, form. The actual structures of the two forms of phenolphthalein are shown in Fig. 15.6.

To see how molecules such as phenolphthalein function as indicators, consider the following equilibrium for some hypothetical indicator HIn, a weak acid with $K_a = 1.0 \times 10^{-8}$.



The indicator phenolphthalein is colorless in acidic solution and pink in basic solution.



By rearranging, we get

$$\frac{K_a}{[\text{H}^+]} = \frac{[\text{In}^-]}{[\text{HIn}]}$$

Suppose we add a few drops of this indicator to an acidic solution whose pH is 1.0 ($[\text{H}^+] = 1.0 \times 10^{-1}$). Then

$$\frac{K_a}{[\text{H}^+]} = \frac{1.0 \times 10^{-8}}{1.0 \times 10^{-1}} = 10^{-7} = \frac{1}{10,000,000} = \frac{[\text{In}^-]}{[\text{HIn}]}$$

The *end point* is defined by the change in color of the indicator. The *equivalence point* is defined by the reaction stoichiometry.

This ratio shows that the predominant form of the indicator is HIn, resulting in a red solution. As OH[−] is added to this solution in a titration, [H⁺] decreases and the equilibrium shifts to the right, changing HIn to In[−]. At some point in a titration, enough of the In[−] form will be present in the solution so that a purple tint will be noticeable. That is, a color change from red to reddish purple will occur.

How much In[−] must be present for the human eye to detect that the color is different from the original one? For most indicators, about a tenth of the initial form must be converted to the other form before a new color is apparent. We will assume, then, that in the titration of an acid with a base, the color change will occur at a pH where

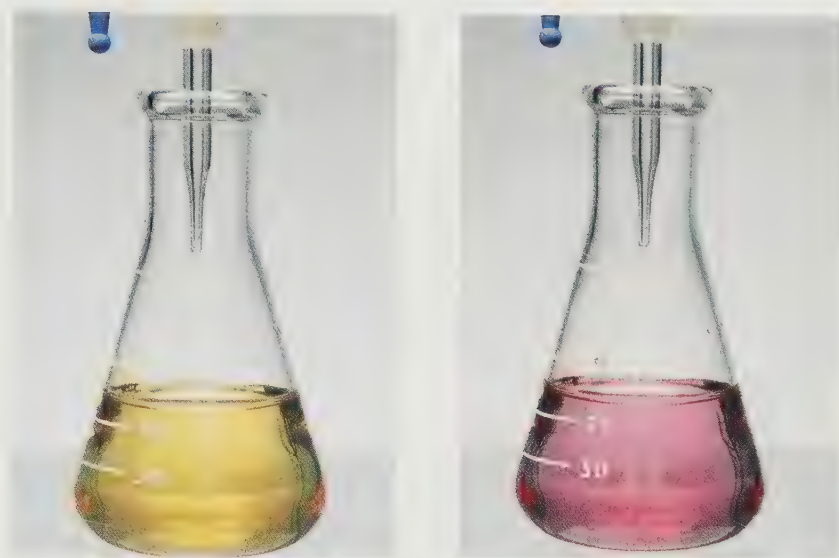
$$\frac{[\text{In}^-]}{[\text{HIn}]} = \frac{1}{10}$$

SAMPLE EXERCISE 15.11

Indicator Color Change

Bromthymol blue, an indicator with a K_a value of 1.0×10^{-7} , is yellow in its HIn form and blue in its In[−] form. Suppose we put a few drops of this indicator in a strongly acidic solution. If the solution is then titrated with NaOH, at what pH will the indicator color change first be visible?

Methyl orange indicator is yellow in basic solution and red in acidic solution.



SOLUTION

For bromthymol blue,

$$K_a = 1.0 \times 10^{-7} = \frac{[\text{H}^+][\text{In}^-]}{[\text{HIn}]}$$

We assume that the color change is visible when

$$\frac{[\text{In}^-]}{[\text{HIn}]} = \frac{1}{10}$$

That is, we assume that we can see the first hint of a greenish tint (yellow plus a little blue) when the solution contains 1 part blue and 10 parts yellow (see Fig. 15.7).

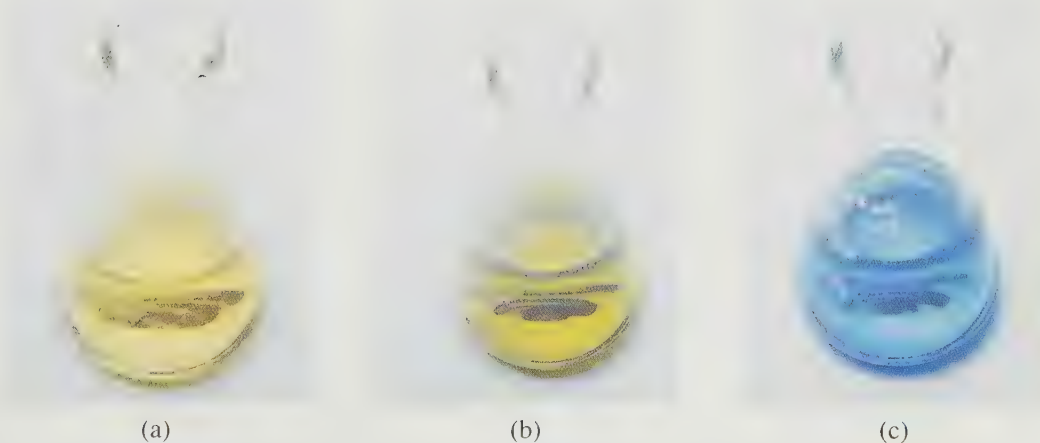


FIGURE 15.7

(a) Yellow acid form of bromthymol blue; (b) a greenish tint is seen when the solution contains 1 part blue and 10 parts yellow; (c) blue basic form.

Thus

$$K_a = 1.0 \times 10^{-7} = \frac{[\text{H}^+](1)}{10}$$

$$[\text{H}^+] = 1.0 \times 10^{-6} \quad \text{or} \quad \text{pH} = 6.00$$

The color change is first visible at pH 6.00.

See Exercises 15.65 and 15.66.

The Henderson–Hasselbalch equation is very useful in determining the pH at which an indicator changes color. For example, application of Equation (15.2) to the K_a expression for the general indicator HIn yields

$$\text{pH} = \text{p}K_a + \log\left(\frac{[\text{In}^-]}{[\text{HIn}]}\right)$$

where K_a is the dissociation constant for the acid form of the indicator (HIn). Since we assume that the color change is visible when

$$\frac{[\text{In}^-]}{[\text{HIn}]} = \frac{1}{10}$$

we have the following equation for determining the pH at which the color change occurs:

$$\text{pH} = \text{p}K_a + \log\left(\frac{1}{10}\right) = \text{p}K_a - 1$$

For bromthymol blue ($K_a = 1 \times 10^{-7}$, or $\text{p}K_a = 7$), the pH at the color change is

$$\text{pH} = 7 - 1 = 6$$

as we calculated in Sample Exercise 15.11.

When a basic solution is titrated, the indicator HIn will initially exist as In^- in solution, but as acid is added, more HIn will be formed. In this case the color change will be visible when there is a mixture of 10 parts In^- and 1 part HIn. That is, a color change from blue to blue-green will occur (see Fig. 15.7) due to the presence of some of the yellow HIn molecules. This color change will be first visible when

$$\frac{[\text{In}^-]}{[\text{HIn}]} = \frac{10}{1}$$

Note that this is the reciprocal of the ratio for the titration of an acid. Substituting this ratio into the Henderson–Hasselbalch equation gives

$$\text{pH} = \text{p}K_a + \log\left(\frac{10}{1}\right) = \text{p}K_a + 1$$

For bromthymol blue ($\text{p}K_a = 7$), we have a color change at

$$\text{pH} = 7 + 1 = 8$$

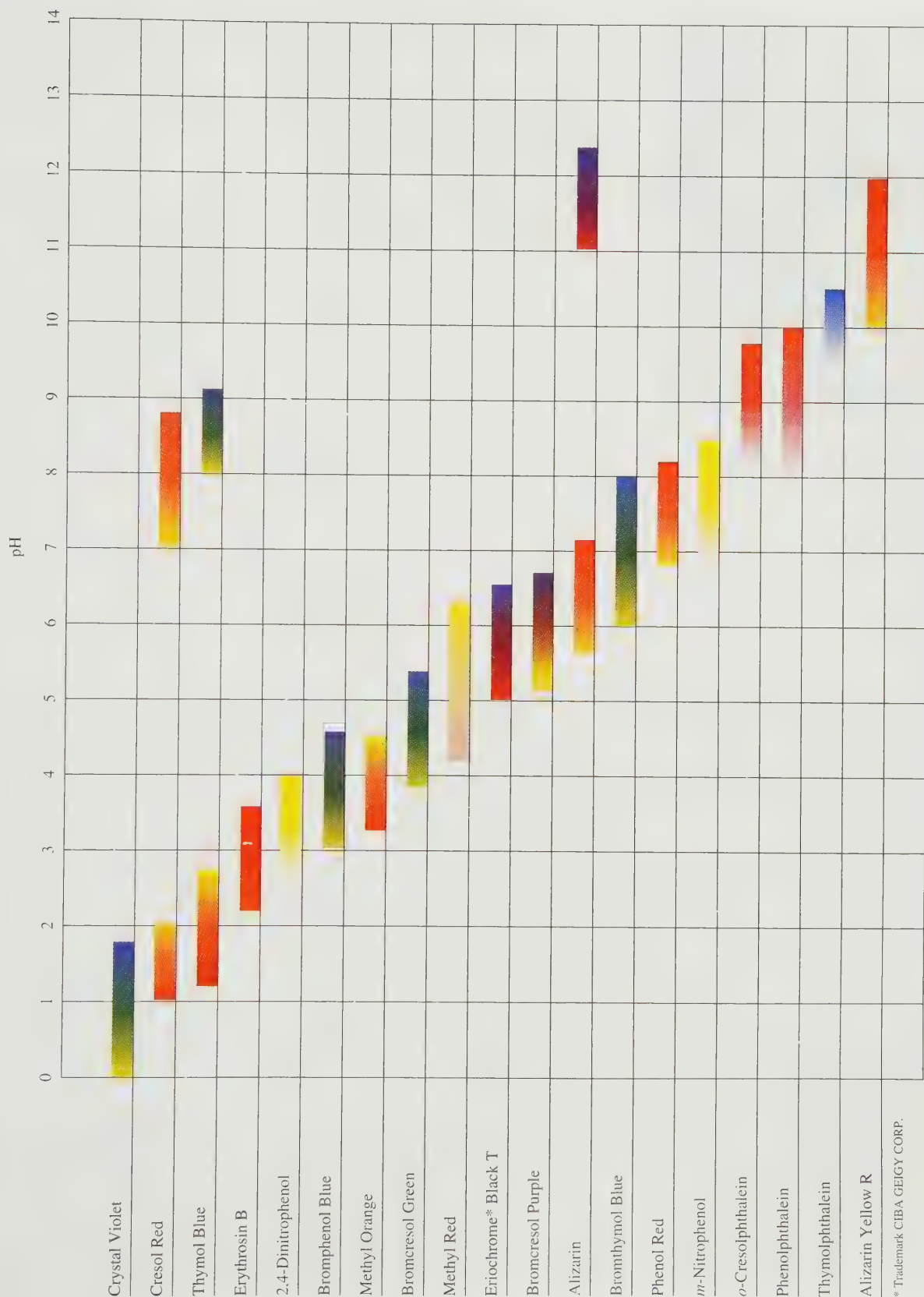
In summary, when bromthymol blue is used for the titration of an acid, the starting form will be HIn (yellow), and the color change occurs at a pH of about 6. When bromthymol blue is used for the titration of a base, the starting form is In^- (blue), and the color change occurs at a pH of about 8. Thus the useful pH range for bromthymol blue is

$$\text{p}K_a(\text{bromthymol blue}) \pm 1 = 7 \pm 1$$

or from 6 to 8. This is a general result. For a typical acid–base indicator with dissociation constant K_a , the color transition occurs over a range of pH values given by $\text{p}K_a \pm 1$. The useful pH ranges for several common indicators are shown in Fig. 15.8.

FIGURE 15.8

The useful pH ranges for several common indicators. Note that most indicators have a useful range of about two pH units, as predicted by the expression $pK_a \pm 1$.



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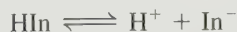
The pH ranges shown are approximate. Specific transition ranges depend on the indicator solvent chosen.



Universal indicator paper can be used to estimate the pH of a solution.

When we choose an indicator for a titration, we want the indicator end point (where the color changes) and the titration equivalence point to be as close as possible. Choosing an indicator is easier if there is a large change in pH near the equivalence point of the titration. The dramatic change in pH near the equivalence point in a strong acid–strong base titration (Figs. 15.1 and 15.2) produces a sharp end point; that is, the complete color change (from the acid-to-base or base-to-acid colors) usually occurs over one drop of added titrant.

What indicator should we use for the titration of 100.00 mL of 0.100 *M* HCl with 0.100 *M* NaOH? We know that the equivalence point occurs at pH 7.00. In the initially acidic solution, the indicator will be predominantly in the HIn form. As OH[−] ions are added, the pH increases rather slowly at first (see Fig. 15.1) and then rises rapidly at the equivalence point. This sharp change causes the indicator dissociation equilibrium



to shift suddenly to the right, producing enough In[−] ions to give a color change. Since we are titrating an acid, the indicator is predominantly in the acid form initially. Therefore, the first observable color change will occur at a pH where

$$\frac{[\text{In}^-]}{[\text{HIn}]} = \frac{1}{10}$$

$$\text{Thus} \quad \text{pH} = \text{p}K_a + \log\left(\frac{1}{10}\right) = \text{p}K_a - 1$$

If we want an indicator that changes color at pH 7, we can use this relationship to find the *pK_a* value for a suitable indicator:

$$\text{pH} = 7 = \text{p}K_a - 1 \quad \text{or} \quad \text{p}K_a = 7 + 1 = 8$$

Thus an indicator with a *pK_a* value of 8 (*K_a* = 1 × 10^{−8}) changes color at about pH 7 and is ideal for marking the end point for a strong acid–strong base titration.

How crucial is it for a strong acid–strong base titration that the indicator change color exactly at pH 7? We can answer this question by examining the pH change near the equivalence point of the titration of 100 mL of 0.10 *M* HCl and 0.10 *M* NaOH. The data for a few points at or near the equivalence point are shown in Table 15.3. Note that in going from 99.99 to 100.01 mL of added NaOH solution (about half of a drop), the pH changes from 5.3 to 8.7—a very dramatic change. This behavior leads to the following general conclusions about indicators for a strong acid–strong base titration:

Indicator color changes will be sharp, occurring with the addition of a single drop of titrant.

There is a wide choice of suitable indicators. The results will agree within one drop of titrant, using indicators with end points as far apart as pH 5 and pH 9 (see Fig. 15.9).

The titration of weak acids is somewhat different. Figure 15.4 shows that the weaker the acid being titrated, the smaller the vertical area around the equivalence point. This allows much less flexibility in choosing the indicator. We must choose an indicator whose useful pH range has a midpoint as close as possible to the pH at the equivalence point. For example, we saw earlier that in the titration of 0.1 *M* HC₂H₃O₂ with 0.1 *M* NaOH the pH at the equivalence point is 8.7 (see Fig. 15.3). A good indicator choice would be phenolphthalein, since its useful pH range is 8

TABLE 15.3
Selected pH Values Near the Equivalence Point in the Titration of 100.0 mL of 0.10 *M* HCl with 0.10 *M* NaOH

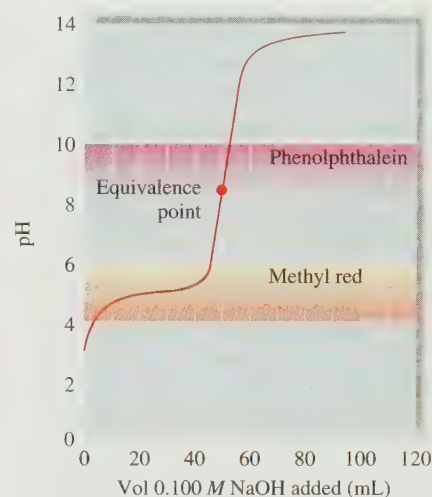
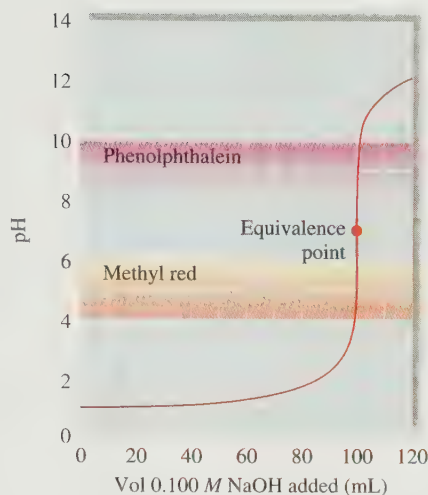
NaOH Added (mL)	pH
99.99	5.3
100.00	7.0
100.01	8.7

FIGURE 15.9 (Left)

The pH curve for the titration of 100.0 mL of 0.10 M HCl with 0.10 M NaOH. Note that the end points of phenolphthalein and methyl red occur at virtually the same amounts of added NaOH.

FIGURE 15.10 (Right)

The pH curve for the titration of 50 mL of 0.1 M $\text{HC}_2\text{H}_3\text{O}_2$ with 0.1 M NaOH. Phenolphthalein will give an end point very close to the equivalence point of the titration. Methyl red would change color well before the equivalence point (so the end point would be very different from the equivalence point) and would not be a suitable indicator for this titration.



to 10. Thymol blue (changes color, pH 8–9) also would be acceptable, but methyl red would not. The choice of an indicator is illustrated graphically in Fig. 15.10.

Solubility Equilibria

15.6 Solubility Equilibria and the Solubility Product

Solubility is a very important phenomenon. The fact that substances such as sugar and table salt dissolve in water allows us to flavor foods easily. The fact that calcium sulfate is less soluble in hot water than in cold water causes it to coat tubes in boilers, reducing thermal efficiency. Tooth decay involves solubility: When food lodges between the teeth, acids form that dissolve tooth enamel, which contains a mineral called *hydroxyapatite*, $\text{Ca}_5(\text{PO}_4)_3\text{OH}$. Tooth decay can be reduced by treating teeth with fluoride (see Chemical Impact, p. 755). Fluoride replaces the hydroxide in hydroxyapatite to produce the corresponding fluorapatite, $\text{Ca}_5(\text{PO}_4)_3\text{F}$, and calcium fluoride, CaF_2 , both of which are less soluble in acids than the original enamel. Another important consequence of solubility involves the use of a suspension of barium sulfate to improve the clarity of X rays of the gastrointestinal tract. The very low solubility of barium sulfate, which contains the toxic ion Ba^{2+} , makes ingestion of the compound safe.

In this section we consider the equilibria associated with solids dissolving to form aqueous solutions. We will assume that when a typical ionic solid dissolves in water, it dissociates completely into separate hydrated cations and anions. For example, calcium fluoride dissolves in water as follows:



When the solid salt is first added to the water, no Ca^{2+} and F^{-} ions are present. However, as the dissolution proceeds, the concentrations of Ca^{2+} and F^{-} increase, making it more and more likely that these ions will collide and re-form the solid

Adding F^{-} to drinking water is controversial. See Geoff Rayner-Canham, "Fluoride: Trying to Separate Fact From Fallacy," *Chem 73 News*, Sept. 2001, pp. 16–19.

For simplicity, we will ignore the effects of ion associations in these solutions.



An X ray of the lower gastrointestinal tract using barium sulfate.

Pure liquids and pure solids are never included in an equilibrium expression (Section 13.4).

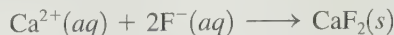


Visualization: Supersaturated Sodium Acetate

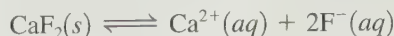
K_{sp} is an equilibrium constant; solubility is an equilibrium position.

SAMPLE EXERCISE 15.12

phase. Thus two competing processes are occurring—the dissolution reaction and its reverse:



Ultimately, dynamic equilibrium is reached:



At this point no more solid dissolves (the solution is said to be *saturated*).

We can write an equilibrium expression for this process according to the law of mass action:

$$K_{sp} = [\text{Ca}^{2+}][\text{F}^{-}]^2$$

where $[\text{Ca}^{2+}]$ and $[\text{F}^{-}]$ are expressed in mol/L. The constant K_{sp} is called the **solubility product constant** or simply the **solubility product** for the equilibrium expression.

Since CaF_2 is a pure solid, it is not included in the equilibrium expression. The fact that the amount of excess solid present does not affect the position of the solubility equilibrium might seem strange at first; more solid means more surface area exposed to the solvent, which would seem to result in greater solubility. This is not the case, however. When the ions in solution re-form the solid, they do so on the surface of the solid. Thus doubling the surface area of the solid not only doubles the rate of dissolving, it also doubles the rate of re-formation of the solid. The amount of excess solid present therefore has no effect on the equilibrium position. Similarly, although either increasing the surface area by grinding up the solid or stirring the solution speeds up the attainment of equilibrium, neither procedure changes the amount of solid dissolved at equilibrium. Neither the amount of excess solid nor the size of the particles present will shift the *position* of the solubility equilibrium.

It is very important to distinguish between the *solubility* of a given solid and its *solubility product*. The solubility product is an *equilibrium constant* and has only *one* value for a given solid at a given temperature. Solubility, on the other hand, is an *equilibrium position*. In pure water at a specific temperature a given salt has a particular solubility. On the other hand, if a common ion is present in the solution, the solubility varies according to the concentration of the common ion. However, in all cases the product of the ion concentrations must satisfy the K_{sp} expression. The K_{sp} values at 25°C for many common ionic solids are listed in Table 15.4. The units are customarily omitted.

Solving solubility equilibria problems requires many of the same procedures we have used to deal with acid–base equilibria, as illustrated in Sample Exercises 15.12 and 15.13.

Calculating K_{sp} from Solubility I

Copper(I) bromide has a measured solubility of 2.0×10^{-4} mol/L at 25°C. Calculate its K_{sp} value.

SOLUTION

In this experiment the solid was placed in contact with water. Thus, before any reaction occurred, the system contained solid CuBr and H_2O . The process that occurs is the dissolving of CuBr to form the separated Cu^{+} and Br^{-} ions:



where

$$K_{sp} = [\text{Cu}^{+}][\text{Br}^{-}]$$

TABLE 15.4 K_{sp} Values at 25°C for Common Ionic Solids

Ionic Solid	K_{sp} (at 25°C)	Ionic Solid	K_{sp} (at 25°C)	Ionic Solid	K_{sp} (at 25°C)	
Fluorides						
BaF ₂	2.4×10^{-5}	Hg ₂ CrO ₄ *	2×10^{-9}	Co(OH) ₂	2.5×10^{-16}	
MgF ₂	6.4×10^{-9}	BaCrO ₄	8.5×10^{-11}	Ni(OH) ₂	1.6×10^{-16}	
PbF ₂	4×10^{-8}	Ag ₂ CrO ₄	9.0×10^{-12}	Zn(OH) ₂	4.5×10^{-17}	
SrF ₂	7.9×10^{-10}	PbCrO ₄	2×10^{-16}	Cu(OH) ₂	1.6×10^{-19}	
CaF ₂	4.0×10^{-11}	Carbonates		Hg(OH) ₂	3×10^{-26}	
Chlorides						
PbCl ₂	1.6×10^{-5}		NiCO ₃	1.4×10^{-7}	Sn(OH) ₂	3×10^{-27}
AgCl	1.6×10^{-10}		CaCO ₃	8.7×10^{-9}	Cr(OH) ₃	6.7×10^{-31}
Hg ₂ Cl ₂ *	1.1×10^{-18}		BaCO ₃	1.6×10^{-9}	Al(OH) ₃	2×10^{-32}
Bromides						
PbBr ₂	4.6×10^{-6}	SrCO ₃	7×10^{-10}	Fe(OH) ₃	4×10^{-38}	
AgBr	5.0×10^{-13}	CuCO ₃	2.5×10^{-10}	Co(OH) ₃	2.5×10^{-43}	
Hg ₂ Br ₂ *	1.3×10^{-22}	ZnCO ₃	2×10^{-10}	Sulfides		
Iodides						
PbI ₂	1.4×10^{-8}	MnCO ₃	8.8×10^{-11}		MnS	2.3×10^{-13}
AgI	1.5×10^{-16}	FeCO ₃	2.1×10^{-11}		FeS	3.7×10^{-19}
Hg ₂ I ₂ *	4.5×10^{-29}	Ag ₂ CO ₃	8.1×10^{-12}		NiS	3×10^{-21}
Sulfates						
CaSO ₄	6.1×10^{-5}	CdCO ₃	5.2×10^{-12}	CoS	5×10^{-22}	
Ag ₂ SO ₄	1.2×10^{-5}	PbCO ₃	1.5×10^{-15}	ZnS	2.5×10^{-22}	
SrSO ₄	3.2×10^{-7}	MgCO ₃	6.8×10^{-6}	SnS	1×10^{-26}	
PbSO ₄	1.3×10^{-8}	Hg ₂ CO ₃ *	9.0×10^{-15}	CdS	1.0×10^{-28}	
BaSO ₄	1.5×10^{-9}	Hydroxides		PbS	7×10^{-29}	
Chromates						
SrCrO ₄	3.6×10^{-5}		Ba(OH) ₂	5.0×10^{-3}	CuS	8.5×10^{-45}
			Sr(OH) ₂	3.2×10^{-4}	Ag ₂ S	1.6×10^{-49}
			Ca(OH) ₂	1.3×10^{-6}	HgS	1.6×10^{-54}
		AgOH	2.0×10^{-8}	Phosphates		
		Mg(OH) ₂	8.9×10^{-12}		Ag ₃ PO ₄	1.8×10^{-18}
		Mn(OH) ₂	2×10^{-13}		Sr ₃ (PO ₄) ₂	1×10^{-31}
		Cd(OH) ₂	5.9×10^{-15}		Ca ₃ (PO ₄) ₂	1.3×10^{-32}
		Pb(OH) ₂	1.2×10^{-15}		Ba ₃ (PO ₄) ₂	6×10^{-39}
		Fe(OH) ₂	1.8×10^{-15}	Pb ₃ (PO ₄) ₂	1×10^{-54}	

*Contains Hg₂²⁺ ions. $K = [\text{Hg}_2^{2+}][\text{X}^-]^2$ for Hg₂X₂ salts, for example.

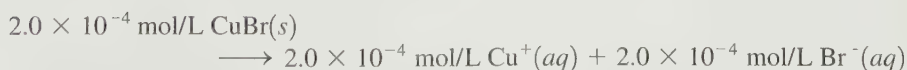
Initially, the solution contains no Cu⁺ or Br⁻, so the initial concentrations are

$$[\text{Cu}^+]_0 = [\text{Br}^-]_0 = 0$$

The equilibrium concentrations can be obtained from the measured solubility of CuBr, which is 2.0×10^{-4} mol/L. This means that 2.0×10^{-4} mol solid CuBr dissolves per 1.0 L of solution to come to equilibrium with the excess solid. The reaction is



Thus



We can now write the equilibrium concentrations:

$$\begin{aligned} [\text{Cu}^+] &= [\text{Cu}^+]_0 + \text{change to reach equilibrium} \\ &= 0 + 2.0 \times 10^{-4} \text{ mol/L} \end{aligned}$$

$$\begin{aligned}\text{and} \quad [\text{Br}^-] &= [\text{Br}^-]_0 + \text{change to reach equilibrium} \\ &= 0 + 2.0 \times 10^{-4} \text{ mol/L}\end{aligned}$$

These equilibrium concentrations allow us to calculate the value of K_{sp} for CuBr:

$$\begin{aligned}K_{\text{sp}} &= [\text{Cu}^+][\text{Br}^-] = (2.0 \times 10^{-4} \text{ mol/L})(2.0 \times 10^{-4} \text{ mol/L}) \\ &= 4.0 \times 10^{-8} \text{ mol}^2/\text{L}^2 = 4.0 \times 10^{-8}\end{aligned}$$

The units for K_{sp} values are usually omitted.

See Exercise 15.75.

SAMPLE EXERCISE 15.13



Precipitation of bismuth sulfide.

Sulfide is a very basic anion and really exists in water as HS^- . We will not consider this complication.

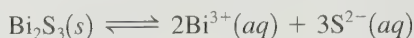
Solubilities must be expressed in mol/L in K_{sp} calculations.

Calculating K_{sp} from Solubility II

Calculate the K_{sp} value for bismuth sulfide (Bi_2S_3), which has a solubility of 1.0×10^{-15} mol/L at 25°C .

SOLUTION

The system initially contains H_2O and solid Bi_2S_3 , which dissolves as follows:



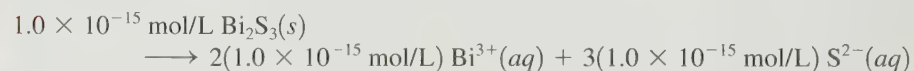
Therefore,

$$K_{\text{sp}} = [\text{Bi}^{3+}]^2[\text{S}^{2-}]^3$$

Since no Bi^{3+} and S^{2-} ions were present in solution before the Bi_2S_3 dissolved,

$$[\text{Bi}^{3+}]_0 = [\text{S}^{2-}]_0 = 0$$

Thus the equilibrium concentrations of these ions will be determined by the amount of salt that dissolves to reach equilibrium, which in this case is 1.0×10^{-15} mol/L. Since each Bi_2S_3 unit contains 2Bi^{3+} and 3S^{2-} ions:



The equilibrium concentrations are

$$[\text{Bi}^{3+}] = [\text{Bi}^{3+}]_0 + \text{change} = 0 + 2.0 \times 10^{-15} \text{ mol/L}$$

$$[\text{S}^{2-}] = [\text{S}^{2-}]_0 + \text{change} = 0 + 3.0 \times 10^{-15} \text{ mol/L}$$

Then

$$K_{\text{sp}} = [\text{Bi}^{3+}]^2[\text{S}^{2-}]^3 = (2.0 \times 10^{-15})^2(3.0 \times 10^{-15})^3 = 1.1 \times 10^{-73}$$

See Exercises 15.76 through 15.78.

We have seen that the experimentally determined solubility of an ionic solid can be used to calculate its K_{sp} value.* The reverse is also possible: The solubility of an ionic solid can be calculated if its K_{sp} value is known.

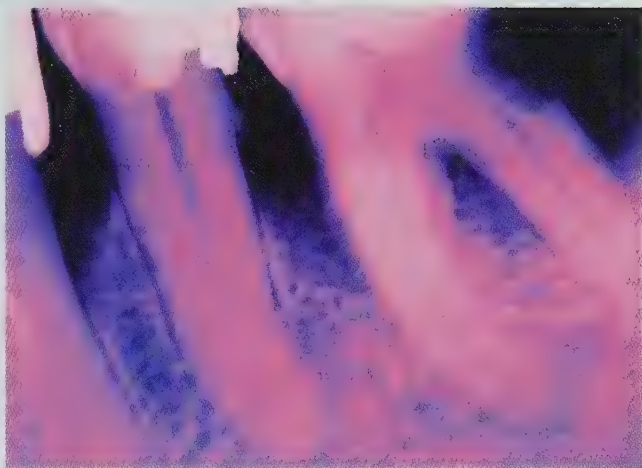
* This calculation assumes that all the dissolved solid is present as separated ions. In some cases, such as CaSO_4 , large numbers of ion pairs exist in solution, so this method yields an incorrect value for K_{sp} .

CHEMICAL IMPACT

The Chemistry of Teeth

If dental chemistry continues to progress at the present rate, tooth decay may soon be a thing of the past. Cavities are holes that develop in tooth enamel, which is composed of the mineral hydroxyapatite, $\text{Ca}_5(\text{PO}_4)_3\text{OH}$. Recent research has shown that there is constant dissolving and re-forming of the tooth mineral in the saliva at the tooth's surface. Demineralization (dissolving of tooth enamel) is mainly caused by weak acids in the saliva created by bacteria as they metabolize carbohydrates in food. (The solubility of $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ in acidic saliva should come as no surprise to you if you understand how pH affects the solubility of a salt with basic anions.)

In the first stages of tooth decay, parts of the tooth surface become porous and spongy and develop swiss-cheese-like holes that, if untreated, eventually turn into cavities (see photo). However, recent results indicate that if the affected tooth is bathed in a solution containing appropriate amounts of Ca^{2+} , PO_4^{3-} , and F^- , it remineralizes. Because the F^- replaces OH^- in the tooth mineral ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$ is changed to $\text{Ca}_5(\text{PO}_4)_3\text{F}$), the remineralized area is more resistant to future decay, since fluoride is a weaker base than hydroxide ion. In addition, it has been shown that the presence of Sr^{2+} in the remineralizing fluid significantly increases resistance to decay.



X-ray photo showing decay (dark area) on the molar (right).

If these results hold up under further study, the work of dentists will change dramatically. Dentists will be much more involved in preventing damage to teeth than in repairing damage that has already occurred. One can picture the routine use of a remineralization rinse that will repair problem areas before they become cavities. Dental drills could join leeches as a medical anachronism.

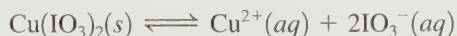
SAMPLE EXERCISE 15.14

Calculating Solubility from K_{sp}

The K_{sp} value for copper(II) iodate, $\text{Cu}(\text{IO}_3)_2$, is 1.4×10^{-7} at 25°C . Calculate its solubility at 25°C .

SOLUTION

The system initially contains H_2O and solid $\text{Cu}(\text{IO}_3)_2$, which dissolves according to the following equilibrium:



Therefore,

$$K_{sp} = [\text{Cu}^{2+}][\text{IO}_3^-]^2$$

To find the solubility of $\text{Cu}(\text{IO}_3)_2$, we must find the equilibrium concentrations of the Cu^{2+} and IO_3^- ions. We do this in the usual way by specifying the initial concentrations (before any solid has dissolved) and then defining the change required to reach equilibrium. Since in this case we do not know the solubility, we will assume that x mol/L of the solid dissolves to reach equilibrium. The 1:2 stoichiometry of the salt means that



The concentrations are as follows:

Initial Concentration (mol/L) (Before Any $\text{Cu}(\text{IO}_3)_2$ Dissolves)		Equilibrium Concentration (mol/L)
$[\text{Cu}^{2+}]_0 = 0$ $[\text{IO}_3^-]_0 = 0$	$x \text{ mol/L}$ dissolves to reach equilibrium $\rightarrow$	$[\text{Cu}^{2+}] = x$ $[\text{IO}_3^-] = 2x$

Substituting the equilibrium concentrations into the expression for K_{sp} gives

$$1.4 \times 10^{-7} = K_{\text{sp}} = [\text{Cu}^{2+}][\text{IO}_3^-]^2 = (x)(2x)^2 = 4x^3$$

Then
$$x = \sqrt[3]{3.5 \times 10^{-8}} = 3.3 \times 10^{-3} \text{ mol/L}$$

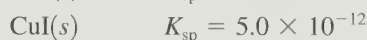
Thus the solubility of solid $\text{Cu}(\text{IO}_3)_2$ is $3.3 \times 10^{-3} \text{ mol/L}$.

See Exercises 15.79 and 15.80.

Relative Solubilities

A salt's K_{sp} value gives us information about its solubility. However, we must be careful in using K_{sp} values to predict the *relative* solubilities of a group of salts. There are two possible cases:

1. The salts being compared produce the same number of ions. For example, consider



Each of these solids dissolves to produce two ions:



$$K_{\text{sp}} = [\text{cation}][\text{anion}]$$

If x is the solubility in mol/L, then at equilibrium

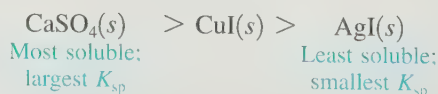
$$[\text{Cation}] = x$$

$$[\text{Anion}] = x$$

$$K_{\text{sp}} = [\text{cation}][\text{anion}] = x^2$$

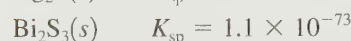
$$x = \sqrt{K_{\text{sp}}} = \text{solubility}$$

Therefore, in this case we can compare the solubilities for these solids by comparing the K_{sp} values:



2. The salts being compared produce different numbers of ions. For example, consider

Salt	K_{sp}	Calculated Solubility (mol/L)
CuS	8.5×10^{-45}	9.2×10^{-23}
Ag ₂ S	1.6×10^{-49}	3.4×10^{-17}
Bi ₂ S ₃	1.1×10^{-73}	1.0×10^{-15}


$$\text{Bi}_2\text{S}_3(s) > \text{Ag}_2\text{S}(s) > \text{CuS}(s)$$

Most soluble Least soluble

Remember that relative solubilities can be predicted by comparing K_{sp} values *only* for salts that produce the same total number of ions.

So far we have considered ionic solids dissolved in pure water. We will now see what happens when the water contains an ion in common with the dissolving salt. For example, consider the solubility of solid silver chromate (Ag_2CrO_4 , $K_{\text{sp}} = 9.0 \times 10^{-12}$) in a 0.100 *M* solution of AgNO_3 . Before any Ag_2CrO_4 dissolves, the solution contains the major species Ag^+ , NO_3^- , and H_2O , with solid Ag_2CrO_4 on the bottom of the container. Since NO_3^- is not found in Ag_2CrO_4 , we can ignore it. The relevant initial concentrations (before any Ag_2CrO_4 dissolves) are

$$[\text{CrO}_4^{2-}]_0 = 0$$

$$\text{Ag}_2\text{CrO}_4(s) \rightleftharpoons 2\text{Ag}^+(aq) + \text{CrO}_4^{2-}(aq)$$
$$K_{\text{sp}} = [\text{Ag}^+]^2[\text{CrO}_4^{2-}] = 9.0 \times 10^{-12}$$
$$x \text{ mol/L Ag}_2\text{CrO}_4(s) \longrightarrow 2x \text{ mol/L Ag}^+(aq) + x \text{ mol/L CrO}_4^{2-}$$
$$[\text{CrO}_4^{2-}] = [\text{CrO}_4^{2-}]_0 + \text{change} = 0 + x = x$$


A potassium chromate solution being added to aqueous silver nitrate, forming silver chromate.

Substituting these concentrations into the expression for K_{sp} gives

$$9.0 \times 10^{-12} = [\text{Ag}^+]^2[\text{CrO}_4^{2-}] = (0.100 + 2x)^2(x)$$

The mathematics required here appear to be complicated, since the multiplication of terms on the right-hand side produces an expression that contains an x^3 term. However, as is usually the case, we can make simplifying assumptions. Since the K_{sp} value for Ag_2CrO_4 is small (the position of the equilibrium lies far to the left), x is expected to be small compared with 0.100 M . Therefore, $0.100 + 2x \approx 0.100$, which allows simplification of the expression:

$$9.0 \times 10^{-12} = (0.100 + 2x)^2(x) \approx (0.100)^2(x)$$

Then
$$x \approx \frac{9.0 \times 10^{-12}}{(0.100)^2} = 9.0 \times 10^{-10} \text{ mol/L}$$

Since x is much less than 0.100 M , the approximation is valid (by the 5% rule). Thus

$$\text{Solubility of } \text{Ag}_2\text{CrO}_4 \text{ in } 0.100\text{ M } \text{AgNO}_3 = x = 9.0 \times 10^{-10} \text{ mol/L}$$

and the equilibrium concentrations are

$$[\text{Ag}^+] = 0.100 + 2x = 0.100 + 2(9.0 \times 10^{-10}) = 0.100\text{ M}$$

$$[\text{CrO}_4^{2-}] = x = 9.0 \times 10^{-10}\text{ M}$$

Now we compare the solubilities of Ag_2CrO_4 in pure water and in $0.100\text{ M } \text{AgNO}_3$:

$$\text{Solubility of } \text{Ag}_2\text{CrO}_4 \text{ in pure water} = 1.3 \times 10^{-4} \text{ mol/L}$$

$$\text{Solubility of } \text{Ag}_2\text{CrO}_4 \text{ in } 0.100\text{ M } \text{AgNO}_3 = 9.0 \times 10^{-10} \text{ mol/L}$$

Note that the solubility of Ag_2CrO_4 is much less in the presence of Ag^+ ions from AgNO_3 . This is another example of the common ion effect. The solubility of a solid is lowered if the solution already contains ions common to the solid.

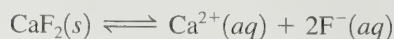
SAMPLE EXERCISE 15.15

Solubility and Common Ions

Calculate the solubility of solid CaF_2 ($K_{sp} = 4.0 \times 10^{-11}$) in a 0.025 M NaF solution.

SOLUTION

Before any CaF_2 dissolves, the solution contains the major species Na^+ , F^- , and H_2O . The solubility equilibrium for CaF_2 is



and
$$K_{sp} = 4.0 \times 10^{-11} = [\text{Ca}^{2+}][\text{F}^-]^2$$

Initial Concentration (mol/L) (Before any CaF_2 Dissolves)		Equilibrium Concentration (mol/L)
$[\text{Ca}^{2+}]_0 = 0$	$x \text{ mol/L } \text{CaF}_2$ $\xrightarrow[\text{to reach}]{\text{dissolves}}$ equilibrium	$[\text{Ca}^{2+}] = x$
$[\text{F}^-]_0 = 0.025\text{ M}$		$[\text{F}^-] = 0.025 + 2x$
From $0.025\text{ M } \text{NaF}$		From NaF From CaF_2

Substituting the equilibrium concentrations into the expression for K_{sp} gives

$$K_{\text{sp}} = 4.0 \times 10^{-11} = [\text{Ca}^{2+}][\text{F}^-]^2 = (x)(0.025 + 2x)^2$$

Assuming that $2x$ is negligible compared with 0.025 (since K_{sp} is small) gives

$$\begin{aligned} 4.0 \times 10^{-11} &\approx (x)(0.025)^2 \\ x &\approx 6.4 \times 10^{-8} \end{aligned}$$

The approximation is valid (by the 5% rule), and

$$\text{Solubility} = x = 6.4 \times 10^{-8} \text{ mol/L}$$

Thus 6.4×10^{-8} mol solid CaF_2 dissolves per liter of the 0.025 M NaF solution.

See Exercises 15.85 through 15.88.

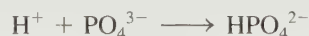
pH and Solubility

The pH of a solution can greatly affect a salt's solubility. For example, magnesium hydroxide dissolves according to the equilibrium



Addition of OH^- ions (an increase in pH) will, by the common ion effect, force the equilibrium to the left, decreasing the solubility of $\text{Mg}(\text{OH})_2$. On the other hand, an addition of H^+ ions (a decrease in pH) increases the solubility, because OH^- ions are removed from solution by reacting with the added H^+ ions. In response to the lower concentration of OH^- , the equilibrium position moves to the right. This is why a suspension of solid $\text{Mg}(\text{OH})_2$, known as *milk of magnesia*, dissolves as required in the stomach to combat excess acidity.

This idea also applies to salts with other types of anions. For example, the solubility of silver phosphate (Ag_3PO_4) is greater in acid than in pure water because the PO_4^{3-} ion is a strong base that reacts with H^+ to form the HPO_4^{2-} ion. The reaction



occurs in acidic solution, thus lowering the concentration of PO_4^{3-} and shifting the solubility equilibrium



to the right. This, in turn, increases the solubility of silver phosphate.

Silver chloride (AgCl), however, has the same solubility in acid as in pure water. Why? Since the Cl^- ion is a very weak base (that is, HCl is a very strong acid), no HCl molecules are formed. Thus the addition of H^+ to a solution containing Cl^- does not affect $[\text{Cl}^-]$ and has no effect on the solubility of a chloride salt.

The general rule is that if the anion X^- is an effective base—that is, if HX is a weak acid—the salt MX will show increased solubility in an acidic solution. Examples of common anions that are effective bases are OH^- , S^{2-} , CO_3^{2-} , $\text{C}_2\text{O}_4^{2-}$, and CrO_4^{2-} . Salts containing these anions are much more soluble in an acidic solution than in pure water.

As mentioned at the beginning of this chapter, one practical result of the increased solubility of carbonates in acid is the formation of huge limestone caves such as Mammoth Cave in Kentucky and Carlsbad Caverns in New Mexico. Carbon

dioxide dissolved in groundwater makes it acidic, increasing the solubility of calcium carbonate and eventually producing huge caverns. As the carbon dioxide escapes to the air, the pH of the dripping water goes up and the calcium carbonate precipitates, forming stalactites and stalagmites.

15.7 Precipitation and Qualitative Analysis

So far we have considered solids dissolving in solutions. Now we will consider the reverse process—the formation of a solid from solution. When solutions are mixed, various reactions can occur. We have already considered acid–base reactions in some detail. In this section we show how to predict whether a precipitate will form when two solutions are mixed. We will use the **ion product**, which is defined just like the expression for K_{sp} for a given solid except that *initial concentrations are used* instead of equilibrium concentrations. For solid CaF_2 , the expression for the ion product Q is written

$$Q = [\text{Ca}^{2+}]_0[\text{F}^-]_0^2$$

If we add a solution containing Ca^{2+} ions to a solution containing F^- ions, a precipitate may or may not form, depending on the concentrations of these ions in the resulting mixed solution. To predict whether precipitation will occur, we consider the relationship between Q and K_{sp} .

If Q is greater than K_{sp} , precipitation occurs and will continue until the concentrations are reduced to the point that they satisfy K_{sp} .

If Q is less than K_{sp} , no precipitation occurs.

Q is used here in a very similar way to the use of the reaction quotient in Chapter 13.

SAMPLE EXERCISE 15.16

Determining Precipitation Conditions

A solution is prepared by adding 750.0 mL of $4.00 \times 10^{-3} \text{ M}$ $\text{Ce}(\text{NO}_3)_3$ to 300.0 mL of $2.00 \times 10^{-2} \text{ M}$ KIO_3 . Will $\text{Ce}(\text{IO}_3)_3$ ($K_{sp} = 1.9 \times 10^{-10}$) precipitate from this solution?

SOLUTION

First, we calculate $[\text{Ce}^{3+}]_0$ and $[\text{IO}_3^-]_0$ in the mixed solution before any reaction occurs:

$$[\text{Ce}^{3+}]_0 = \frac{(750.0 \text{ mL})(4.00 \times 10^{-3} \text{ mmol/mL})}{(750.0 + 300.0) \text{ mL}} = 2.86 \times 10^{-3} \text{ M}$$

$$[\text{IO}_3^-]_0 = \frac{(300.0 \text{ mL})(2.00 \times 10^{-2} \text{ mmol/mL})}{(750.0 + 300.0) \text{ mL}} = 5.71 \times 10^{-3} \text{ M}$$

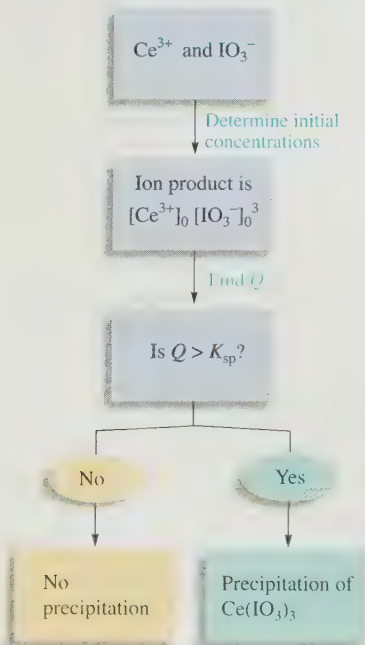
The ion product for $\text{Ce}(\text{IO}_3)_3$ is

$$Q = [\text{Ce}^{3+}]_0[\text{IO}_3^-]_0^3 = (2.86 \times 10^{-3})(5.71 \times 10^{-3})^3 = 5.32 \times 10^{-10}$$

Since Q is greater than K_{sp} , $\text{Ce}(\text{IO}_3)_3$ will precipitate from the mixed solution.

See Exercises 15.91 and 15.92.

Sometimes we want to do more than simply predict whether precipitation will occur; we may want to calculate the equilibrium concentrations in the solution after precipitation occurs. For example, let us calculate the equilibrium concentrations



For $\text{Ce}(\text{IO}_3)_3(s)$, $K_{\text{sp}} = [\text{Ce}^{3+}][\text{IO}_3^-]^3$.

of Pb^{2+} and I^- ions in a solution formed by mixing 100.0 mL of 0.0500 M $\text{Pb}(\text{NO}_3)_2$ and 200.0 mL of 0.100 M NaI. First, we must determine whether solid PbI_2 ($K_{\text{sp}} = 1.4 \times 10^{-8}$) forms when the solutions are mixed. To do so, we need to calculate $[\text{Pb}^{2+}]_0$ and $[\text{I}^-]_0$ before any reaction occurs:

$$[\text{Pb}^{2+}]_0 = \frac{\text{mmol Pb}^{2+}}{\text{mL solution}} = \frac{(100.0 \text{ mL})(0.0500 \text{ mmol/mL})}{300.0 \text{ mL}} = 1.67 \times 10^{-2} M$$

$$[\text{I}^-]_0 = \frac{\text{mmol I}^-}{\text{mL solution}} = \frac{(200.0 \text{ mL})(0.100 \text{ mmol/mL})}{300.0 \text{ mL}} = 6.67 \times 10^{-2} M$$

The ion product for PbI_2 is

$$Q = [\text{Pb}^{2+}]_0[\text{I}^-]_0^2 = (1.67 \times 10^{-2})(6.67 \times 10^{-2})^2 = 7.43 \times 10^{-5}$$

Since Q is greater than K_{sp} , a precipitate of PbI_2 will form.

Since the K_{sp} for PbI_2 is quite small (1.4×10^{-8}), only very small quantities of Pb^{2+} and I^- can coexist in aqueous solution. In other words, when Pb^{2+} and I^- are mixed, most of these ions will precipitate out as PbI_2 . That is, the reaction



(which is the reverse of the dissolution reaction) goes essentially to completion.

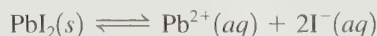
If, when two solutions are mixed, a reaction occurs that goes virtually to completion, it is essential to do the stoichiometry calculations before considering the equilibrium calculations. Therefore, in this case we let the system go completely in the direction toward which it tends. Then we will let it adjust back to equilibrium. If we let Pb^{2+} and I^- react to completion, we have the following concentrations:

	Pb^{2+}	+	2I^-	$\longrightarrow$	PbI_2
Before reaction:	(100.0 mL)(0.0500 M) = 5.00 mmol		(200.0 mL)(0.100 M) = 20.0 mmol		The amount of PbI_2 formed does not influence the equilibrium.
After reaction:	0 mmol		$20.0 - 2(5.00)$ = 10.0 mmol		

In this reaction 10 mmol I^- is in excess.

Next we must allow the system to adjust to equilibrium. At equilibrium $[\text{Pb}^{2+}]$ is not actually zero because the reaction does not go quite to completion. The best way to think about this is that once the PbI_2 is formed, a very small amount redissolves to reach equilibrium. Since I^- is in excess, the PbI_2 is dissolving into a solution that contains 10.0 mmol I^- per 300.0 mL of solution, or $3.33 \times 10^{-2} M \text{I}^-$.

We could state this problem as follows: What is the solubility of solid PbI_2 in a $3.33 \times 10^{-2} M$ NaI solution? The lead iodide dissolves according to the equation



The concentrations are as follows:

Initial Concentration (mol/L)		Equilibrium Concentration (mol/L)
$[\text{Pb}^{2+}]_0 = 0$ $[\text{I}^-]_0 = 3.33 \times 10^{-2}$	$\xrightarrow[\text{dissolves}]{\text{PbI}_2(s)}$ $x \text{ mol/L}$	$[\text{Pb}^{2+}] = x$ $[\text{I}^-] = 3.33 \times 10^{-2} + 2x$

Substituting into the expression for K_{sp} gives

$$K_{sp} = 1.4 \times 10^{-8} = [\text{Pb}^{2+}][\text{I}^-]^2 = (x)(3.33 \times 10^{-2} + 2x)^2 \approx (x)(3.33 \times 10^{-2})^2$$

Then $[\text{Pb}^{2+}] = x = 1.3 \times 10^{-5} M$

$$[\text{I}^-] = 3.33 \times 10^{-2} M$$

Note that $3.33 \times 10^{-2} \gg 2x$, so the approximation is valid. These Pb^{2+} and I^- concentrations thus represent the equilibrium concentrations present in a solution formed by mixing 100.0 mL of 0.0500 M $\text{Pb}(\text{NO}_3)_2$ and 200.0 mL of 0.100 M NaI.

SAMPLE EXERCISE 15.17

Precipitation

A solution is prepared by mixing 150.0 mL of $1.00 \times 10^{-2} M$ $\text{Mg}(\text{NO}_3)_2$ and 250.0 mL of $1.00 \times 10^{-1} M$ NaF. Calculate the concentrations of Mg^{2+} and F^- at equilibrium with solid MgF_2 ($K_{sp} = 6.4 \times 10^{-9}$).

SOLUTION

The first step is to determine whether solid MgF_2 forms. To do this, we need to calculate the concentrations of Mg^{2+} and F^- in the mixed solution and find Q :

$$[\text{Mg}^{2+}]_0 = \frac{\text{mmol Mg}^{2+}}{\text{mL solution}} = \frac{(150.0 \text{ mL})(1.00 \times 10^{-2} M)}{400.0 \text{ mL}} = 3.75 \times 10^{-3} M$$

$$[\text{F}^-]_0 = \frac{\text{mmol F}^-}{\text{mL solution}} = \frac{(250.0 \text{ mL})(1.00 \times 10^{-1} M)}{400.0 \text{ mL}} = 6.25 \times 10^{-2} M$$

$$Q = [\text{Mg}^{2+}]_0 [\text{F}^-]_0^2 = (3.75 \times 10^{-3})(6.25 \times 10^{-2})^2 = 1.46 \times 10^{-5}$$

Since Q is greater than K_{sp} , solid MgF_2 will form.

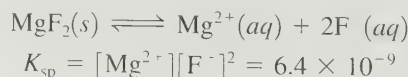
The next step is to run the precipitation reaction to completion:

	Mg^{2+}	+	2F^-	$\longrightarrow$	$\text{MgF}_2(s)$
Before reaction:	$(150.0)(1.00 \times 10^{-2})$ $= 1.50 \text{ mmol}$		$(250.0)(1.00 \times 10^{-1})$ $= 25.0 \text{ mmol}$		
After reaction:	$1.50 - 1.50 = 0$		$25.0 - 2(1.50)$ $= 22.0 \text{ mmol}$		

Note that excess F^- remains after the precipitation reaction goes to completion. The concentration is

$$[\text{F}^-]_{\text{excess}} = \frac{22.0 \text{ mmol}}{400.0 \text{ mL}} = 5.50 \times 10^{-2} M$$

Although we have assumed that the Mg^{2+} is completely consumed, we know that $[\text{Mg}^{2+}]$ will not be zero at equilibrium. We can compute the equilibrium $[\text{Mg}^{2+}]$ by letting MgF_2 redissolve to satisfy the expression for K_{sp} . How much MgF_2 will dissolve in a $5.50 \times 10^{-2} M$ NaF solution? We proceed as usual:



$\text{Mg}^{2+}, \text{F}^-$

Find initial concentrations

$[\text{Mg}^{2+}]_0 = 3.75 \times 10^{-3} M$
 $[\text{F}^-]_0 = 6.25 \times 10^{-2} M$

Find Q

$Q = [\text{Mg}^{2+}]_0 [\text{F}^-]_0^2 = 1.46 \times 10^{-5}$

$Q > K_{sp}$

$\text{Mg}^{2+} + 2\text{F}^- \rightarrow \text{MgF}_2(s)$

Run reaction to completion

Mg^{2+} is limiting
 F^- is in excess

Calculate concentrations of excess F^-

$[\text{F}^-]_{\text{excess}} = 5.50 \times 10^{-2} M$

Determine $[\text{Mg}^{2+}]$ and $[\text{F}^-]$ at equilibrium

$K_{sp} = [\text{Mg}^{2+}][\text{F}^-]^2$
 $6.4 \times 10^{-9} = (x)(5.50 \times 10^{-2} + 2x)^2$

$[\text{Mg}^{2+}] = 2.1 \times 10^{-6} M$
 $[\text{F}^-] = 5.50 \times 10^{-2} M$

Initial Concentration (mol/L)		Equilibrium Concentration (mol/L)
$[\text{Mg}^{2+}]_0 = 0$	$x \text{ mol/L}$	$[\text{Mg}^{2+}] = x$
$[\text{F}^-]_0 = 5.50 \times 10^{-2}$	$\xrightarrow[\text{dissolves}]{\text{MgF}_2(s)}$	$[\text{F}^-] = 5.50 \times 10^{-2} + 2x$

$$\begin{aligned}
 K_{\text{sp}} &= 6.4 \times 10^{-9} = [\text{Mg}^{2+}][\text{F}^-]^2 \\
 &= (x)(5.50 \times 10^{-2} + 2x)^2 \approx (x)(5.50 \times 10^{-2})^2 \\
 [\text{Mg}^{2+}] &= x = 2.1 \times 10^{-6} \text{ M} \\
 [\text{F}^-] &= 5.50 \times 10^{-2} \text{ M}
 \end{aligned}$$

See Exercises 15.93 and 15.94.

The approximations made here fall within the 5% rule.

Selective Precipitation

Mixtures of metal ions in aqueous solution are often separated by **selective precipitation**, that is, by using a reagent whose anion forms a precipitate with only one or a few of the metal ions in the mixture. For example, suppose we have a solution containing both Ba^{2+} and Ag^+ ions. If NaCl is added to the solution, AgCl precipitates as a white solid, but since BaCl_2 is soluble, the Ba^{2+} ions remain in solution.

SAMPLE EXERCISE 15.18

Selective Precipitation

A solution contains $1.0 \times 10^{-4} \text{ M Cu}^+$ and $2.0 \times 10^{-3} \text{ M Pb}^{2+}$. If a source of I^- is added gradually to this solution, will PbI_2 ($K_{\text{sp}} = 1.4 \times 10^{-8}$) or CuI ($K_{\text{sp}} = 5.3 \times 10^{-12}$) precipitate first? Specify the concentration of I^- necessary to begin precipitation of each salt.

SOLUTION

For PbI_2 , the K_{sp} expression is

$$1.4 \times 10^{-8} = K_{\text{sp}} = [\text{Pb}^{2+}][\text{I}^-]^2$$

Since $[\text{Pb}^{2+}]$ in this solution is known to be $2.0 \times 10^{-3} \text{ M}$, the greatest concentration of I^- that can be present without causing precipitation of PbI_2 can be calculated from the K_{sp} expression:

$$\begin{aligned}
 1.4 \times 10^{-8} &= [\text{Pb}^{2+}][\text{I}^-]^2 = (2.0 \times 10^{-3})[\text{I}^-]^2 \\
 [\text{I}^-] &= 2.6 \times 10^{-3} \text{ M}
 \end{aligned}$$

Any I^- in excess of this concentration will cause solid PbI_2 to form.

Similarly, for CuI , the K_{sp} expression is

$$5.3 \times 10^{-12} = K_{\text{sp}} = [\text{Cu}^+][\text{I}^-] = (1.0 \times 10^{-4})[\text{I}^-]$$

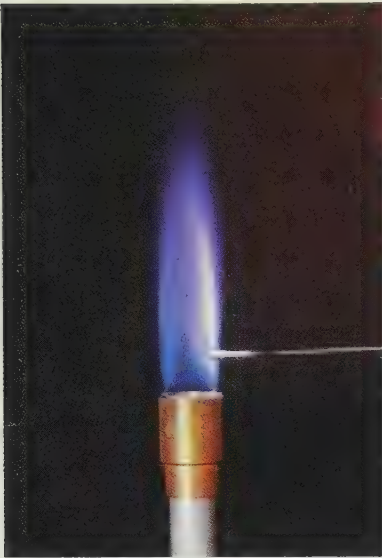
and

$$[\text{I}^-] = 5.3 \times 10^{-8} \text{ M}$$

A concentration of I^- in excess of $5.3 \times 10^{-8} \text{ M}$ will cause formation of solid CuI .

As I^- is added to the mixed solution, CuI will precipitate first, since the $[\text{I}^-]$ required is less. Therefore, Cu^+ would be separated from Pb^{2+} using this reagent.

See Exercises 15.95 and 15.96.



Flame test for potassium.

We can compare K_{sp} values to find relative solubilities because FeS and MnS produce the same number of ions in solution.

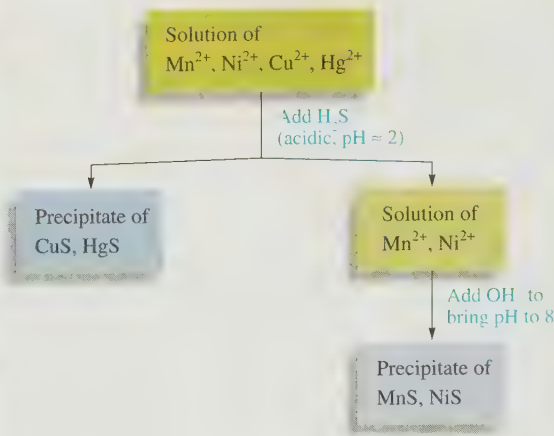


FIGURE 15.11
 The separation of Cu^{2+} and Hg^{2+} from Ni^{2+} and Mn^{2+} using H_2S . At a low pH, $[\text{S}^{2-}]$ is relatively low and only the very insoluble HgS and CuS precipitate. When OH^- is added to lower $[\text{H}^+]$, the value of $[\text{S}^{2-}]$ increases, and MnS and NiS precipitate.

Since metal sulfide salts differ dramatically in their solubilities, the sulfide ion is often used to separate metal ions by selective precipitation. For example, consider a solution containing a mixture of $10^{-3} \text{ M Fe}^{2+}$ and $10^{-3} \text{ M Mn}^{2+}$. Since FeS ($K_{sp} = 3.7 \times 10^{-19}$) is much less soluble than MnS ($K_{sp} = 2.3 \times 10^{-13}$), careful addition of S^{2-} to the mixture will precipitate Fe^{2+} as FeS , leaving Mn^{2+} in solution.

One real advantage of the sulfide ion as a precipitating reagent is that because it is basic, its concentration can be controlled by regulating the pH of the solution. H_2S is a diprotic acid that dissociates in two steps:



Note from the small K_{a2} value that S^{2-} ions have a high affinity for protons. In an acidic solution (large $[\text{H}^+]$), $[\text{S}^{2-}]$ will be relatively small, since under these conditions the dissociation equilibria will lie far to the left. On the other hand, in basic solutions $[\text{S}^{2-}]$ will be relatively large, since the very small value of $[\text{H}^+]$ will pull both equilibria to the right, producing S^{2-} .

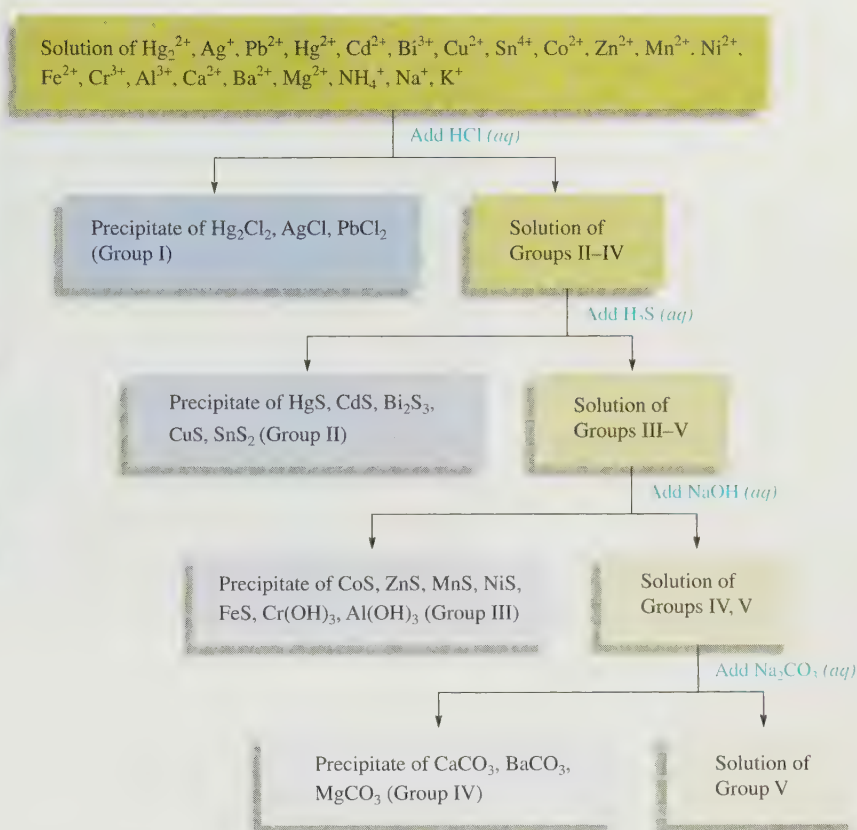
This means that the most insoluble sulfide salts, such as CuS ($K_{sp} = 8.5 \times 10^{-45}$) and HgS ($K_{sp} = 1.6 \times 10^{-54}$), can be precipitated from an acidic solution, leaving the more soluble ones, such as MnS ($K_{sp} = 2.3 \times 10^{-13}$) and NiS ($K_{sp} = 3 \times 10^{-21}$), still dissolved. The manganese and nickel sulfides can then be precipitated by making the solution slightly basic. This procedure is diagramed in Fig. 15.11.

Qualitative Analysis

The classic scheme for **qualitative analysis** of a mixture containing all the common cations (listed in Fig. 15.12) involves first separating them into five major groups based on solubilities. (These groups are not directly related to the groups of the periodic table.) Each group is then treated further to separate and identify the individual ions. We will be concerned here only with separation of the major groups.



Flame test for sodium.

**FIGURE 15.12**

A schematic diagram of the classic method for separating the common cations by selective precipitation.

Group I—Insoluble chlorides

When dilute aqueous HCl is added to a solution containing a mixture of the common cations, only Ag^+ , Pb^{2+} , and Hg_2^{2+} will precipitate out as insoluble chlorides. All other chlorides are soluble and remain in solution. The Group I precipitate is removed, leaving the other ions in solution for treatment with sulfide ion.

Group II—Sulfides insoluble in acid solution

After the insoluble chlorides are removed, the solution is still acidic, since HCl was added. If H_2S is added to this solution, only the most insoluble sulfides (those of Hg^{2+} , Cd^{2+} , Bi^{3+} , Cu^{2+} , and Sn^{4+}) will precipitate, since $[\text{S}^{2-}]$ is relatively low because of the high concentration of H^+ . The more soluble sulfides will remain dissolved under these conditions, and the precipitate of the insoluble salt is removed.

Group III—Sulfides insoluble in basic solution

The solution is made basic at this stage, and more H_2S is added. As we saw earlier, a basic solution produces a higher $[\text{S}^{2-}]$, which leads to precipitation of the more soluble sulfides. The cations precipitated as sulfides at this stage are Co^{2+} , Zn^{2+} , Mn^{2+} , Ni^{2+} , and Fe^{2+} . If any Cr^{3+} and Al^{3+} ions are present, they also will precipitate, but as insoluble hydroxides (remember the solution is now basic). The precipitate is separated from the solution containing the rest of the ions.



From left to right, cadmium sulfide, chromium(III) hydroxide, aluminum hydroxide, and nickel(II) hydroxide.

Group IV—Insoluble carbonates

At this point, all the cations have been precipitated except those from Groups 1A and 2A of the periodic table. The Group 2A cations form insoluble carbonates and can be precipitated by the addition of CO_3^{2-} . For example, Ba^{2+} , Ca^{2+} , and Mg^{2+} form solid carbonates and can be removed from the solution.

Group V—Alkali metal and ammonium ions

The only ions remaining in solution at this point are the Group 1A cations and the NH_4^+ ion, all of which form soluble salts with the common anions. The Group 1A cations are usually identified by the characteristic colors they produce when heated in a flame. These colors are due to the emission spectra of these ions.

The qualitative analysis scheme for cations based on the selective precipitation procedure described above is summarized in Fig. 15.12.

Complex Ion Equilibria

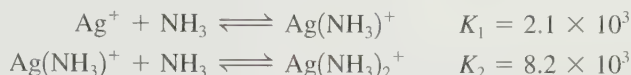
15.8 Equilibria Involving Complex Ions

A **complex ion** is a charged species consisting of a metal ion surrounded by *ligands*. A ligand is simply a Lewis base—a molecule or ion having a lone electron pair that can be donated to an empty orbital on the metal ion to form a covalent bond. Some common ligands are H_2O , NH_3 , Cl^- , and CN^- . The number of ligands attached to a metal ion is called the *coordination number*. The most common coordination numbers are 6, for example, in $\text{Co}(\text{H}_2\text{O})_6^{2+}$ and $\text{Ni}(\text{NH}_3)_6^{2+}$; 4, for example, in CoCl_4^{2-} and $\text{Cu}(\text{NH}_3)_4^{2+}$; and 2, for example, in $\text{Ag}(\text{NH}_3)_2^+$; but others are known.

The properties of complex ions will be discussed in more detail in Chapter 21. For now, we will just look at the equilibria involving these species. Metal ions add

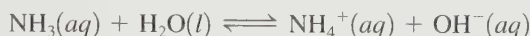


ligands one at a time in steps characterized by equilibrium constants called **formation constants** or **stability constants**. For example, when solutions containing Ag^+ ions and NH_3 molecules are mixed, the following reactions take place:



where K_1 and K_2 are the formation constants for the two steps. In a solution containing Ag^+ and NH_3 , all the species NH_3 , Ag^+ , $\text{Ag}(\text{NH}_3)^+$, and $\text{Ag}(\text{NH}_3)_2^+$ exist at equilibrium. Calculating the concentrations of all these components can be complicated. However, usually the total concentration of the ligand is much larger than the total concentration of the metal ion, and approximations can greatly simplify the problems.

For example, consider a solution prepared by mixing 100.0 mL of 2.0 M NH_3 with 100.0 mL of 1.0×10^{-3} M AgNO_3 . Before any reaction occurs, the mixed solution contains the major species Ag^+ , NO_3^- , NH_3 , and H_2O . What reaction or reactions will occur in this solution? From our discussions of acid–base chemistry, we know that one reaction is



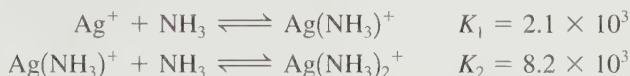
However, we are interested in the reaction between NH_3 and Ag^+ to form complex ions, and since the position of the preceding equilibrium lies far to the left (K_b for NH_3 is 1.8×10^{-5}), we can neglect the amount of NH_3 used up in the reaction with water. Therefore, before any complex ion formation, the concentrations in the mixed solution are

$$[\text{Ag}^+]_0 = \frac{(100.0 \text{ mL})(1.0 \times 10^{-3} \text{ M})}{(200.0 \text{ mL})} = 5.0 \times 10^{-4} \text{ M}$$

↖
Total volume

$$[\text{NH}_3]_0 = \frac{(100.0 \text{ mL})(2.0 \text{ M})}{(200.0 \text{ mL})} = 1.0 \text{ M}$$

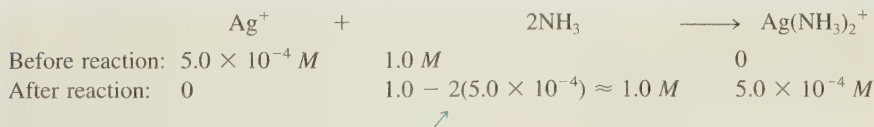
As mentioned already, the Ag^+ ion reacts with NH_3 in a stepwise fashion to form AgNH_3^+ and then $\text{Ag}(\text{NH}_3)_2^+$:



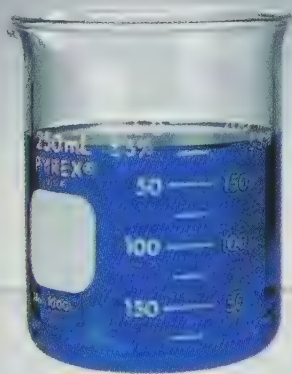
Since both K_1 and K_2 are large, and since there is a large excess of NH_3 , both reactions can be assumed to go essentially to completion. This is equivalent to writing the net reaction in the solution as follows:



The relevant stoichiometric calculations are as follows:



Twice as much NH_3 as
 Ag^+ is required



A solution containing the blue CoCl_4^{2-} complex ion.

Note that in this case we have used molarities when performing the stoichiometry calculations and we have assumed this reaction to be complete, using all the original Ag^+ to form $\text{Ag}(\text{NH}_3)_2^+$. In reality, a *very small amount* of the $\text{Ag}(\text{NH}_3)_2^+$ formed will dissociate to produce small amounts of $\text{Ag}(\text{NH}_3)^+$ and Ag^+ . However, since the amount of $\text{Ag}(\text{NH}_3)_2^+$ dissociating will be so small, we can safely assume that $[\text{Ag}(\text{NH}_3)_2^+]$ is $5.0 \times 10^{-4} \text{ M}$ at equilibrium. Also, we know that since so little NH_3 has been consumed, $[\text{NH}_3]$ is 1.0 M at equilibrium. We can use these concentrations to calculate $[\text{Ag}^+]$ and $[\text{Ag}(\text{NH}_3)^+]$ using the K_1 and K_2 expressions.

To calculate the equilibrium concentration of $\text{Ag}(\text{NH}_3)^+$, we use

$$K_2 = 8.2 \times 10^3 = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}(\text{NH}_3)^+][\text{NH}_3]}$$

since $[\text{Ag}(\text{NH}_3)_2^+]$ and $[\text{NH}_3]$ are known. Rearranging and solving for $[\text{Ag}(\text{NH}_3)^+]$ give

$$[\text{Ag}(\text{NH}_3)^+] = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{K_2[\text{NH}_3]} = \frac{5.0 \times 10^{-4}}{(8.2 \times 10^3)(1.0)} = 6.1 \times 10^{-8} \text{ M}$$

Now the equilibrium concentration of Ag^+ can be calculated using K_1 :

$$K_1 = 2.1 \times 10^3 = \frac{[\text{Ag}(\text{NH}_3)^+]}{[\text{Ag}^+][\text{NH}_3]} = \frac{6.1 \times 10^{-8}}{[\text{Ag}^+](1.0)}$$

$$[\text{Ag}^+] = \frac{6.1 \times 10^{-8}}{(2.1 \times 10^3)(1.0)} = 2.9 \times 10^{-11} \text{ M}$$

So far we have assumed that $\text{Ag}(\text{NH}_3)_2^+$ is the dominant silver-containing species in solution. Is this a valid assumption? The calculated concentrations are

$$\begin{aligned} [\text{Ag}(\text{NH}_3)_2^+] &= 5.0 \times 10^{-4} \text{ M} \\ [\text{Ag}(\text{NH}_3)^+] &= 6.1 \times 10^{-8} \text{ M} \\ [\text{Ag}^+] &= 2.9 \times 10^{-11} \text{ M} \end{aligned}$$

Essentially all the Ag^+ ions originally present end up in $\text{Ag}(\text{NH}_3)_2^+$.

These values clearly support the conclusion that

$$[\text{Ag}(\text{NH}_3)_2^+] \gg [\text{Ag}(\text{NH}_3)^+] \gg [\text{Ag}^+]$$

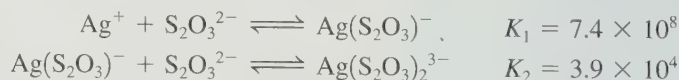
Thus the assumption that $\text{Ag}(\text{NH}_3)_2^+$ is the dominant Ag^+ -containing species is valid, and the calculated concentrations are correct.

This analysis shows that although complex ion equilibria have many species present and look complicated, the calculations are actually quite straightforward, especially if the ligand is present in large excess.

SAMPLE EXERCISE 15.19

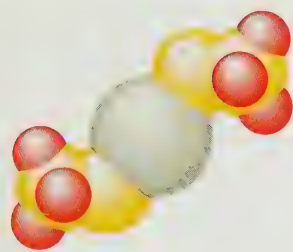
Complex Ions

Calculate the concentrations of Ag^+ , $\text{Ag}(\text{S}_2\text{O}_3)^-$, and $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$ in a solution prepared by mixing 150.0 mL of $1.00 \times 10^{-3} \text{ M}$ AgNO_3 with 200.0 mL of 5.00 M $\text{Na}_2\text{S}_2\text{O}_3$. The stepwise formation equilibria are



SOLUTION

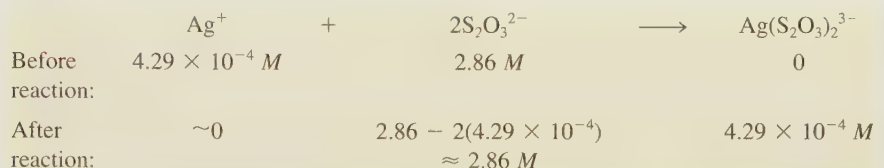
The concentrations of the ligand and metal ion in the mixed solution *before any reaction occurs* are


 $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$

$$[\text{Ag}^+]_0 = \frac{(150.0 \text{ mL})(1.00 \times 10^{-3} \text{ M})}{(150.0 \text{ mL} + 200.0 \text{ mL})} = 4.29 \times 10^{-4} \text{ M}$$

$$[\text{S}_2\text{O}_3^{2-}]_0 = \frac{(200.0 \text{ mL})(5.00 \text{ M})}{(150.0 \text{ mL} + 200.0 \text{ mL})} = 2.86 \text{ M}$$

Since $[\text{S}_2\text{O}_3^{2-}]_0 \gg [\text{Ag}^+]_0$, and since K_1 and K_2 are large, both formation reactions can be assumed to go to completion, and the net reaction in the solution is as follows:



Note that Ag^+ is limiting and that the amount of $\text{S}_2\text{O}_3^{2-}$ consumed is negligible. Also note that since all these species are in the same solution, the molarities can be used to do the stoichiometry problem.

Of course, the concentration of Ag^+ is not zero at equilibrium, and there is some $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$ in the solution. To calculate the concentrations of these species, we must use the K_1 and K_2 expressions. We can calculate the concentration of $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$ from K_2 :

$$3.9 \times 10^4 = K_2 = \frac{[\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}]}{[\text{Ag}(\text{S}_2\text{O}_3)_2^-][\text{S}_2\text{O}_3^{2-}]} = \frac{4.29 \times 10^{-4}}{[\text{Ag}(\text{S}_2\text{O}_3)_2^-](2.86)}$$

$$[\text{Ag}(\text{S}_2\text{O}_3)_2^-] = 3.8 \times 10^{-9} \text{ M}$$

We can calculate $[\text{Ag}^+]$ from K_1 :

$$7.4 \times 10^8 = K_1 = \frac{[\text{Ag}(\text{S}_2\text{O}_3)_2^-]}{[\text{Ag}^+][\text{S}_2\text{O}_3^{2-}]} = \frac{3.8 \times 10^{-9}}{[\text{Ag}^+](2.86)}$$

$$[\text{Ag}^+] = 1.8 \times 10^{-18} \text{ M}$$

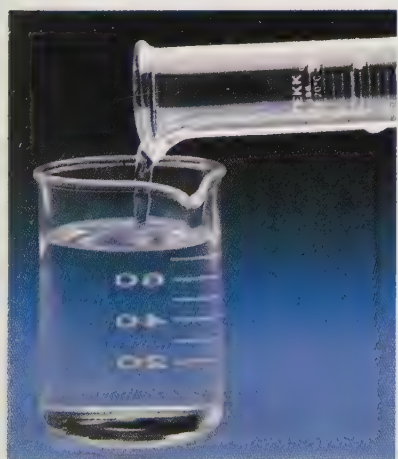
These results show that $[\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}] \gg [\text{Ag}(\text{S}_2\text{O}_3)_2^-] \gg [\text{Ag}^+]$

Thus the assumption is valid that essentially all the original Ag^+ is converted to $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$ at equilibrium.

See Exercises 15.101 and 15.102.

Complex Ions and Solubility

Often ionic solids that are very nearly water-insoluble must be dissolved somehow in aqueous solutions. For example, when the various qualitative analysis groups are precipitated out, the precipitates must be redissolved to separate the ions within each group. Consider a solution of cations that contains Ag^+ , Pb^{2+} , and Hg_2^{2+} , among others. When dilute aqueous HCl is added to this solution, the Group I ions will form the insoluble chlorides AgCl , PbCl_2 , and Hg_2Cl_2 . Once this mixed precipitate is separated from the solution, it must be redissolved to identify the cations individually. How can this be done? We know that some solids are more soluble in acidic than in neutral solutions. What about chloride salts? For example, can AgCl be dissolved by using a strong acid? The answer is no, because Cl^- ions have



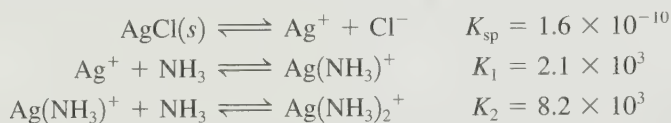
(top) Aqueous ammonia is added to silver chloride (white). (bottom) Silver chloride, insoluble in water, dissolves to form $\text{Ag}(\text{NH}_3)_2^+(aq)$ and $\text{Cl}^-(aq)$.

virtually no affinity for H^+ ions in aqueous solution. The position of the dissolution equilibrium



is not affected by the presence of H^+ .

How can we pull the dissolution equilibrium to the right, even though Cl^- is an extremely weak base? The key is to lower the concentration of Ag^+ in solution by forming complex ions. For example, Ag^+ reacts with excess NH_3 to form the stable complex ion $\text{Ag}(\text{NH}_3)_2^+$. As a result, AgCl is quite soluble in concentrated ammonia solutions. The relevant reactions are



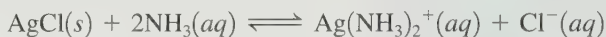
The Ag^+ ion produced by dissolving solid AgCl combines with NH_3 to form $\text{Ag}(\text{NH}_3)_2^+$, which causes more AgCl to dissolve, until the point at which

$$[\text{Ag}^+][\text{Cl}^-] = K_{\text{sp}} = 1.6 \times 10^{-10}$$

Here $[\text{Ag}^+]$ refers only to the Ag^+ ion that is present as a separate species in solution. It is *not* the total silver content of the solution, which is

$$[\text{Ag}]_{\text{total dissolved}} = [\text{Ag}^+] + [\text{Ag}(\text{NH}_3)^+] + [\text{Ag}(\text{NH}_3)_2^+]$$

For reasons discussed in the previous section, virtually all the Ag^+ from the dissolved AgCl ends up in the complex ion $\text{Ag}(\text{NH}_3)_2^+$. Thus we can represent the dissolving of solid AgCl in excess NH_3 by the equation

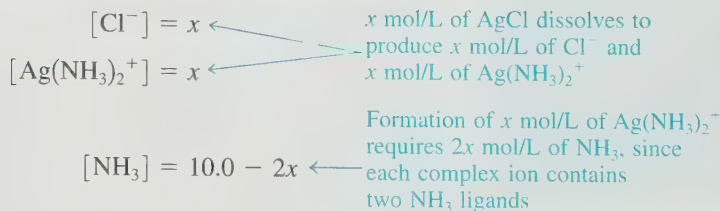


When reactions are added, the equilibrium constant for the overall process is the product of the constants for the individual reactions.

Since this equation is the *sum of the three stepwise reactions* given above, the equilibrium constant for the reaction is the product of the constants for the three reactions. (Demonstrate this to yourself by multiplying together the three expressions for K_{sp} , K_1 , and K_2 .) The equilibrium expression is

$$\begin{aligned}K &= \frac{[\text{Ag}(\text{NH}_3)_2^+][\text{Cl}^-]}{[\text{NH}_3]^2} \\ &= K_{\text{sp}} \times K_1 \times K_2 = (1.6 \times 10^{-10})(2.1 \times 10^3)(8.2 \times 10^3) = 2.8 \times 10^{-3}\end{aligned}$$

Using this expression, we will now calculate the solubility of solid AgCl in a 10.0 M NH_3 solution. If we let x be the solubility (in mol/L) of AgCl in the solution, we can then write the following expressions for the equilibrium concentrations of the pertinent species:



Substituting these concentrations into the equilibrium expression gives

$$K = 2.8 \times 10^{-3} = \frac{[\text{Ag}(\text{NH}_3)_2^+][\text{Cl}^-]}{[\text{NH}_3]^2} = \frac{(x)(x)}{(10.0 - 2x)^2} = \frac{x^2}{(10.0 - 2x)^2}$$

No approximations are necessary here. Taking the square root of both sides of the equation gives

$$\sqrt{2.8 \times 10^{-3}} = \frac{x}{10.0 - 2x}$$

$$x = 0.48 \text{ mol/L} = \text{solubility of AgCl}(s) \text{ in } 10.0 \text{ M NH}_3$$

Thus the solubility of AgCl in 10.0 M NH₃ is much greater than its solubility in pure water, which is

$$\sqrt{K_{\text{sp}}} = 1.3 \times 10^{-5} \text{ mol/L}$$

In this chapter we have considered two strategies for dissolving a water-insoluble ionic solid. If the *anion* of the solid is a good base, the solubility is greatly increased by acidifying the solution. In cases where the anion is not sufficiently basic, the ionic solid often can be dissolved in a solution containing a ligand that forms stable complex ions with its *cation*.

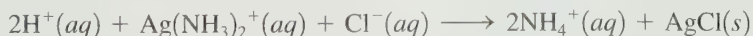
Sometimes solids are so insoluble that combinations of reactions are needed to dissolve them. For example, to dissolve the extremely insoluble HgS ($K_{\text{sp}} = 10^{-54}$), it is necessary to use a mixture of concentrated HCl and concentrated HNO₃, called *aqua regia*. The H⁺ ions in the aqua regia react with the S²⁻ ions to form H₂S, and Cl⁻ reacts with Hg²⁺ to form various complex ions, including HgCl₄²⁻. In addition, NO₃⁻ oxidizes S²⁻ to elemental sulfur. These processes lower the concentrations of Hg²⁺ and S²⁻ and thus promote the solubility of HgS.

Since the solubility of many salts increases with temperature, simple heating is sometimes enough to make a salt sufficiently soluble. For example, earlier in this section we considered the mixed chloride precipitates of the Group I ions—PbCl₂, AgCl, and Hg₂Cl₂. The effect of temperature on the solubility of PbCl₂ is such that we can precipitate PbCl₂ with cold aqueous HCl and then redissolve it by heating the solution to near boiling. The silver and mercury(I) chlorides remain precipitated, since they are not significantly soluble in hot water. However, solid AgCl can be dissolved using aqueous ammonia. The solid Hg₂Cl₂ reacts with NH₃ to form a mixture of elemental mercury and HgNH₂Cl:

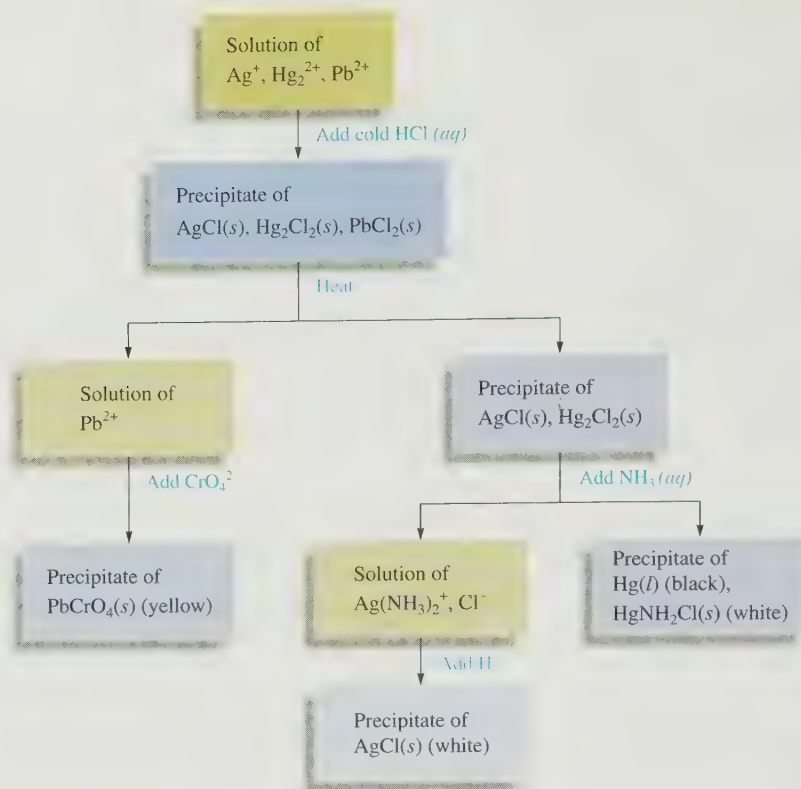


The mixed precipitate appears gray. This is an oxidation–reduction reaction in which one mercury(I) ion in Hg₂Cl₂ is oxidized to Hg²⁺ in HgNH₂Cl and the other mercury(I) ion is reduced to Hg, or elemental mercury.

The treatment of the Group I ions is summarized in Fig. 15.13. Note that the presence of Pb²⁺ is confirmed by adding CrO₄²⁻, which forms bright yellow lead(II) chromate (PbCrO₄). Also note that H⁺ added to a solution containing Ag(NH₃)₂⁺ reacts with the NH₃ to form NH₄⁺, destroying the Ag(NH₃)₂⁺ complex. Silver chloride then re-forms:



Note that the qualitative analysis of cations by selective precipitation involves all the types of reactions we have discussed and represents an excellent application of the principles of chemical equilibrium.

**FIGURE 15.13**

The separation of the Group I ions in the classic scheme of qualitative analysis.

For Review

Summary

Key Terms

Section 15.1

common ion
common ion effect

Section 15.2

buffered solution
Henderson–Hasselbalch equation

Section 15.3

buffering capacity

Section 15.4

pH curve (titration curve)
millimole (mmol)
equivalence point (stoichiometric point)

Section 15.5

acid–base indicator
phenolphthalein

Section 15.6

solubility product constant (solubility product)

When a weak acid HA and its salt NaA are dissolved in the same aqueous solution, a buffering effect is observed. A buffered solution is one that resists a change in pH when either hydroxide ions or protons are added. A buffer may contain a weak acid and its salt or a weak base and its salt. In a buffered solution the pH is governed by the ratio $[\text{A}^-]/[\text{HA}]$. The Henderson–Hasselbalch equation gives the relationship between pH, $\text{p}K_a$, and the ratio $[\text{A}^-]/[\text{HA}]$:

$$\text{pH} = \text{p}K_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$$

The capacity of a buffer depends on the amounts of HA and A^- present. Buffering results because the relatively large amounts of HA and A^- cause the ratio $[\text{A}^-]/[\text{HA}]$ to be almost constant when H^+ or OH^- is added. Optimal buffering results when $[\text{HA}]$ is equal to $[\text{A}^-]$.

The progress of an acid–base titration is often monitored by plotting the pH of the solution versus the volume of added titrant to give a pH curve or titration curve. Strong acid–strong base titrations have a very sharp change in pH near the stoichiometric, or equivalence, point, the point at which the original acid (or base) in the solution has been exactly consumed by the titrant base (or acid). When a weak acid is titrated with a strong base, the shape of the titration curve is quite different. Initially, the curve rises sharply; then it levels off because of the buffering effects of the weak acid and salt mixture. At the equivalence point of a titration of a weak

Section 15.7

ion product
selective precipitation
qualitative analysis

Section 15.8

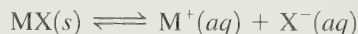
complex ion
formation (stability) constants

acid with a strong base, the pH is greater than 7 because of the basicity of the conjugate base of the weak acid. For a titration of a weak base with a strong acid, the pH at the equivalence point is always less than 7 because of the acidity of the conjugate acid of the weak base. For a strong acid–strong base titration, the pH at the equivalence point equals 7. The equivalence point of a titration is determined by stoichiometry, not by pH.

Another way of following an acid–base titration is by the use of an indicator that marks the end point by changing color. Most commonly used indicators are themselves weak acids and exist in two forms, HIn and In^- , that exhibit different colors. For most indicators, the ratio of the minor form to the major form must be $\frac{1}{10}$ before a color change is apparent. The goal in choosing an indicator is to have the equivalence point and the end point coincide.

The principles of equilibrium also can be applied when a solid dissolves in water. The solubility product K_{sp} is an equilibrium constant defined by the law of mass action. Solubility is an equilibrium position. The K_{sp} value for a salt can be determined by measuring its solubility. The solubility of a salt can be calculated if its K_{sp} value is known.

Addition of an ion common to a salt will push the dissolution equilibrium to the left, reducing the salt's solubility. This is known as the common ion effect. The solubility of a salt MX that is only slightly soluble in pure water can be increased if the solubility equilibrium



can be shifted to the right by lowering $[\text{M}^+]$ or $[\text{X}^-]$. If X^- is a good base, addition of H^+ will form HX and lower $[\text{X}^-]$, thus increasing the salt's solubility. The equilibrium concentration of M^+ can be lowered by adding a ligand to form complex ions with it.

We can predict whether a precipitate will form when two solutions are mixed by using the ion product Q , which is defined just like K_{sp} except that initial concentrations of the ions are used. If Q is greater than K_{sp} , the salt will precipitate.

Mixtures of ions can be separated by selective precipitation, a process in which reagents are added to precipitate single ions or small groups of ions.

In-Class Discussion Questions

These questions are designed to be considered by groups of students in class. Often these questions work well for introducing a particular topic in class.

1. What are the major species in solution after NaHSO_4 is dissolved in water? What happens to the pH of the solution as more NaHSO_4 is added? Why? Would the results vary if baking soda (NaHCO_3) were used instead?
2. A friend asks the following: "Consider a buffered solution made up of the weak acid HA and its salt NaA . If a strong base like NaOH is added, the HA reacts with the OH^- to form A^- . Thus the amount of acid (HA) is decreased, and the amount of base (A^-) is increased. Analogously, adding HCl to the buffered solution forms more of the acid (HA) by reacting with the base (A^-). Thus how can we claim that a buffered solution resists changes in the pH of the solution?" How would you explain buffering to this friend?
3. Mixing together solutions of acetic acid and sodium hydroxide can make a buffered solution. Explain. How does the amount of each solution added change the effectiveness of the buffer? Would a buffer solution made by mixing HCl and NaOH be effective? Explain.
4. Sketch two pH curves, one for the titration of a weak acid with a strong base and one for a strong acid with a strong base. How are they similar? How are they different? Account for the similarities and the differences.
5. Sketch a pH curve for the titration of a weak acid (HA) with a strong base (NaOH). List the major species and explain how you would go about calculating the pH of the solution at various points, including the halfway point and the equivalence point.
6. Devise as many ways as you can to experimentally determine the K_{sp} value of a solid. Explain why each of these would work.
7. You are browsing through the *Handbook of Hypothetical Chemistry* when you come across a solid that is reported to

have a K_{sp} value of zero in water at 25°C. What does this mean?

8. A friend tells you: "The constant K_{sp} of a salt is called the solubility product constant and is calculated from the concentrations of ions in the solution. Thus, if salt A dissolves to a greater extent than salt B, salt A must have a higher K_{sp} than salt B." Do you agree with your friend? Explain.
9. Explain the following phenomenon: You have a test tube with about 20 mL of silver nitrate solution. Upon adding a few drops of sodium chromate solution, you notice a red solid forming in a relatively clear solution. Upon adding a few drops of a sodium chloride solution to the same test tube, you notice a white solid and a pale yellow solution. Use the K_{sp} values in the book to support your explanation, and include the balanced reactions.
10. What happens to the K_{sp} value of a solid as the temperature of the solution changes? Consider both increasing and decreasing temperatures, and explain your answer.
11. Which is more likely to dissolve in an acidic solution, silver sulfide or silver chloride? Why?
12. You have two salts, AgX and AgY , with very similar K_{sp} values. You know that the K_a value for HX is much greater than the K_a value for HY . Which salt is more soluble in an acidic solution? Explain.

A blue question or exercise number indicates that the answer to that question or exercise appears at the back of this book and a solution appears in the *Solutions Guide*.

Questions

13. What is meant by a *common ion*? How does the presence of a common ion affect an equilibrium such as



14. What components must be present to have a buffered solution? For what purposes are buffers used? What is meant by the *capacity* of a buffer? How do the following buffers differ in capacity? How do they differ in pH?

0.01 M acetic acid/0.01 M sodium acetate

0.1 M acetic acid/0.1 M sodium acetate

1.0 M acetic acid/1.0 M sodium acetate

15. Is it necessary that the concentration of the weak acid and weak base in a buffered solution be equal? Explain.
16. Show that the pH at the halfway point of the titration of a weak acid with a strong base is equal to pK_a . Is it possible to determine the K_a of a weak acid from data at points other than the halfway point of a titration?
17. Is it possible for the indicator thymol blue to contain only a single $-CO_2H$ group and no other acidic or basic functional group? Explain.
18. Define the equivalence (stoichiometric) point and the end point of a titration. Why does one choose an indicator so that

the two points coincide? Is it necessary that the pH of the two points be within ± 0.01 pH unit of each other? Explain.

19. Why does an indicator change from its acid to its base color over a range of pH values?
20. Under what circumstances can the relative solubilities of two salts be compared by directly comparing values of their solubility products?

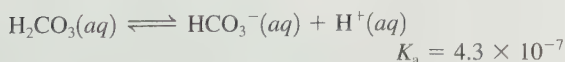
Exercises

In this section similar exercises are paired.

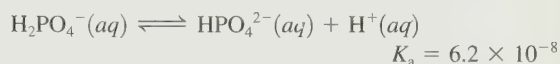
Buffers

21. A certain buffer is made by dissolving $NaHCO_3$ and Na_2CO_3 in some water. Write equations to show how this buffer neutralizes added H^+ and OH^- .
22. A buffer is made by dissolving NH_4Cl and NH_3 in water. Write equations to show how this buffer neutralizes added H^+ and OH^- .
23. Calculate the pH of each of the following solutions.
 - a. 0.100 M propanoic acid ($HC_3H_5O_2$, $K_a = 1.3 \times 10^{-5}$)
 - b. 0.100 M sodium propanoate ($NaC_3H_5O_2$)
 - c. pure H_2O
 - d. A mixture containing 0.100 M $HC_3H_5O_2$ and 0.100 M $NaC_3H_5O_2$
24. Calculate the pH of each of the following solutions.
 - a. 0.100 M $HONH_2$ ($K_b = 1.1 \times 10^{-8}$)
 - b. 0.100 M $HONH_3Cl$
 - c. pure H_2O
 - d. a mixture containing 0.100 M $HONH_2$ and 0.100 M $HONH_3Cl$
25. Compare the percent dissociation of the acid in Exercise 23a with the percent dissociation of the acid in Exercise 23d. Explain the large difference in percent dissociation of the acid.
26. Compare the percent ionization of the base in Exercise 24a with the percent ionization of the base in Exercise 24d. Explain any differences.
27. Calculate the pH after 0.020 mol HCl is added to 1.00 L of each of the four solutions in Exercise 23.
28. Calculate the pH after 0.020 mol HCl is added to 1.00 L of each of the four solutions in Exercise 24.
29. Calculate the pH after 0.020 mol NaOH is added to 1.00 L of each of the four solutions in Exercise 23.
30. Calculate the pH after 0.020 mol NaOH is added to 1.00 L of each of the solutions in Exercise 24.
31. Which of the solutions in Exercise 23 shows the least change in pH upon the addition of acid or base? Explain.
32. Which of the solutions in Exercise 24 is a buffered solution?
33. Calculate the pH of a solution that is 1.00 M HNO_2 and 1.00 M $NaNO_2$.

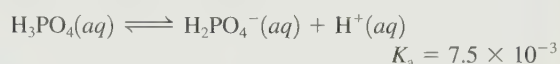
34. Calculate the pH of a solution that is 0.60 M HF and 1.00 M KF.
35. Calculate the pH after 0.10 mol of NaOH is added to 1.00 L of the solution in Exercise 33, and calculate the pH after 0.20 mol of HCl is added to 1.00 L of the solution in Exercise 33.
36. Calculate the pH after 0.10 mol of NaOH is added to 1.00 L of the solution in Exercise 34, and calculate the pH after 0.20 mol of HCl is added to 1.00 L of the solution in Exercise 34.
37. Calculate the pH of each of the following buffered solutions.
- 0.10 M acetic acid/0.25 M sodium acetate
 - 0.25 M acetic acid/0.10 M sodium acetate
 - 0.25 M acetic acid/0.25 M sodium acetate
 - 0.50 M $\text{C}_2\text{H}_5\text{NH}_2$ /0.25 M $\text{C}_2\text{H}_5\text{NH}_3\text{Cl}$
 - 0.50 M $\text{C}_2\text{H}_5\text{NH}_2$ /0.50 M $\text{C}_2\text{H}_5\text{NH}_3\text{Cl}$
38. A buffered solution is made by adding 50.0 g NH_4Cl to 1.00 L of a 0.75 M solution of NH_3 . Calculate the pH of the final solution. (Assume no volume change.)
39. Calculate the pH after 0.010 mol gaseous HCl is added to 250.0 mL of each of the following buffered solutions.
- 0.050 M NH_3 /0.15 M NH_4Cl
 - 0.50 M NH_3 /1.50 M NH_4Cl
- Do the two original buffered solutions differ in their pH or their capacity? What advantage is there in having a buffer with a greater capacity?
40. An aqueous solution contains dissolved $\text{C}_6\text{H}_5\text{NH}_3\text{Cl}$ and $\text{C}_6\text{H}_5\text{NH}_2$. The concentration of $\text{C}_6\text{H}_5\text{NH}_2$ is 0.50 M and pH is 4.20.
- Calculate the concentration of $\text{C}_6\text{H}_5\text{NH}_3^+$ in this buffer solution.
 - Calculate the pH after 4.0 g of NaOH(s) is added to 1.0 L of this solution. (Neglect any volume change.)
41. Calculate the mass of sodium acetate that must be added to 500.0 mL of 0.200 M acetic acid to form a pH = 5.00 buffer solution.
42. What volumes of 0.50 M HNO_2 and 0.50 M NaNO_2 must be mixed to prepare 1.00 L of a solution buffered at pH = 3.55?
43. Consider a solution that contains both $\text{C}_5\text{H}_5\text{N}$ and $\text{C}_5\text{H}_5\text{NHNO}_3$. Calculate the ratio $[\text{C}_5\text{H}_5\text{N}]/[\text{C}_5\text{H}_5\text{NH}^+]$ if the solution has the following pH values.
- pH = 4.50
 - pH = 5.00
 - pH = 5.23
 - pH = 5.50
44. a. Carbonate buffers are important in regulating the pH of blood at 7.40. What is the concentration ratio of CO_2 (usually written H_2CO_3) to HCO_3^- in blood at pH = 7.40?



- b. Phosphate buffers are important in regulating the pH of intracellular fluids at pH values generally between 7.1 and 7.2. What is the concentration ratio of H_2PO_4^- to HPO_4^{2-} in intracellular fluid at pH = 7.15?



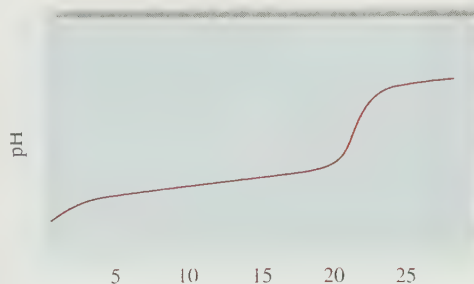
- c. Why is a buffer composed of H_3PO_4 and H_2PO_4^- ineffective in buffering the pH of intracellular fluid?



45. Consider the acids in Table 14.2. Which acid would be the best choice for preparing a pH = 7.00 buffer? Explain how to make 1.0 L of this buffer.
46. Consider the bases in Table 14.3. Which base would be the best choice for preparing a pH = 5.00 buffer? Explain how to make 1.0 L of this buffer.
47. Which of the following mixtures would result in buffered solutions when 1.0 L of each of the two solutions are mixed?
- 0.1 M KOH and 0.1 M $\text{CH}_3\text{NH}_3\text{Cl}$
 - 0.1 M KOH and 0.2 M CH_3NH_2
 - 0.2 M KOH and 0.1 M $\text{CH}_3\text{NH}_3\text{Cl}$
 - 0.1 M KOH and 0.2 M $\text{CH}_3\text{NH}_3\text{Cl}$
48. Which of the following mixtures would result in a buffered solution when 1.0 L of each of the two solutions are mixed?
- 0.2 M HNO_3 and 0.4 M NaNO_3
 - 0.2 M HNO_3 and 0.4 M HF
 - 0.2 M HNO_3 and 0.4 M NaF
 - 0.2 M HNO_3 and 0.4 M NaOH
49. How many moles of NaOH must be added to 1.0 L of 2.0 M $\text{HC}_2\text{H}_3\text{O}_2$ to produce a solution buffered at each pH?
- pH = $\text{p}K_a$
 - pH = 4.00
 - pH = 5.00
50. Calculate the number of moles of HCl(g) that must be added to 1.0 L of 1.0 M $\text{NaC}_2\text{H}_3\text{O}_2$ to produce a solution buffered at each pH.
- pH = $\text{p}K_a$
 - pH = 4.20
 - pH = 5.00

Acid-Base Titrations

51. Consider the titration of a generic weak acid HA with a strong base that gives the following titration curve:



On the curve, indicate the points that correspond to the following:

- the stoichiometric (equivalence) point
- the region with maximum buffering
- $\text{pH} = \text{p}K_a$
- pH depends only on $[\text{HA}]$
- pH depends only on $[\text{A}^-]$
- pH depends only on the amount of excess strong base added

52. Sketch the titration curve for the titration of a generic weak base B with a strong acid. The titration reaction is



On this curve, indicate the points that correspond to the following:

- the stoichiometric (equivalence) point
- the region with maximum buffering
- $\text{pH} = \text{p}K_a$
- pH depends only on $[\text{B}]$
- pH depends only on $[\text{BH}^+]$
- pH depends only on the amount of excess strong acid added

53. Consider the titration of 40.0 mL of 0.200 M HClO_4 by 0.100 M KOH. Calculate the pH of the resulting solution after the following volumes of KOH have been added.

- 0.0 mL
- 10.0 mL
- 40.0 mL
- 80.0 mL
- 100.0 mL

54. Consider the titration of 80.0 mL of 0.100 M $\text{Ba}(\text{OH})_2$ by 0.400 M HCl. Calculate the pH of the resulting solution after the following volumes of HCl have been added.

- 0.0 mL
- 20.0 mL
- 30.0 mL
- 40.0 mL
- 80.0 mL

55. Consider the titration of 100.0 mL of 0.200 M acetic acid ($K_a = 1.8 \times 10^{-5}$) by 0.100 M KOH. Calculate the pH of the resulting solution after the following volumes of KOH have been added.

- 0.0 mL
- 50.0 mL
- 100.0 mL
- 150.0 mL
- 200.0 mL
- 250.0 mL

56. Consider the titration of 100.0 mL of 0.100 M H_2NNH_2 ($K_b = 3.0 \times 10^{-6}$) by 0.200 M HNO_3 . Calculate the pH of the resulting solution after the following volumes of HNO_3 have been added.

- 0.0 mL
- 20.0 mL
- 25.0 mL
- 40.0 mL

- 50.0 mL
- 100.0 mL

57. A 25.0-mL sample of 0.100 M lactic acid ($\text{HC}_3\text{H}_5\text{O}_3$, $\text{p}K_a = 3.86$) is titrated with 0.100 M NaOH solution. Calculate the pH after the addition of 0.0 mL, 4.0 mL, 8.0 mL, 12.5 mL, 20.0 mL, 24.0 mL, 24.5 mL, 24.9 mL, 25.0 mL, 25.1 mL, 26.0 mL, 28.0 mL, and 30.0 mL of the NaOH. Plot the results of your calculations as pH versus milliliters of NaOH added.

58. Repeat the procedure in Exercise 57, but for the titration of 25.0 mL of 0.100 M propanoic acid ($\text{HC}_3\text{H}_5\text{O}_2$, $K_a = 1.3 \times 10^{-5}$) with 0.100 M KOH.

59. Repeat the procedure in Exercise 57, but for the titration of 25.0 mL of 0.100 M NH_3 ($K_b = 1.8 \times 10^{-5}$) with 0.100 M HCl.

60. Repeat the procedure in Exercise 57, but for the titration of 25.0 mL of 0.100 M pyridine with 0.100 M hydrochloric acid (K_b for pyridine is 1.7×10^{-9}). Do not do the points at 24.9 and 25.1 mL.

61. Calculate the pH at the halfway point and at the equivalence point for each of the following titrations.

- 100.0 mL of 0.10 M $\text{HC}_7\text{H}_5\text{O}_2$ ($K_a = 6.4 \times 10^{-5}$) titrated by 0.10 M NaOH
- 100.0 mL of 0.10 M $\text{C}_2\text{H}_5\text{NH}_2$ ($K_b = 5.6 \times 10^{-4}$) titrated by 0.20 M HNO_3
- 100.0 mL of 0.50 M HCl titrated by 0.25 M NaOH

62. In the titration of 50.0 mL of 1.0 M methylamine, CH_3NH_2 ($K_b = 4.4 \times 10^{-4}$), with 0.50 M HCl, calculate the pH under the following conditions.

- after 50.0 mL of 0.50 M HCl has been added
- at the stoichiometric point

63. A sample of a certain monoprotic weak acid was dissolved in water and titrated with 0.125 M NaOH, requiring 16.00 mL to reach the equivalence point. During the titration, the pH after adding 2.00 mL of NaOH was 6.912. Calculate K_a for the weak acid.

64. A sample of an ionic compound NaA, where A^- is the anion of a weak acid, was dissolved in enough water to make 100.0 mL of solution and was then titrated with 0.100 M HCl. After 50.0 mL of HCl was added, the pH was measured and found to be 5.00. The experimenter found that 1.00 L of 0.100 M HCl was required to reach the stoichiometric point of the titration.

- What is the K_b value for A^- ?
- Calculate the pH of the solution at the stoichiometric point of the titration.

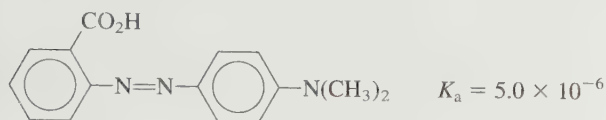
Indicators

65. Two drops of indicator HIn ($K_a = 1.0 \times 10^{-9}$), where HIn is yellow and In^- is blue, are placed in 100.0 mL of 0.10 M HCl.

- What color is the solution initially?
- The solution is titrated with 0.10 M NaOH. At what pH will the color change (yellow to greenish yellow) occur?

- c. What color will the solution be after 200.0 mL of NaOH has been added?

66. Methyl red has the following structure:



It undergoes a color change from red to yellow as a solution gets more basic. Calculate an approximate pH range for which methyl red is useful. What is the color change and the pH at the color change when a weak acid is titrated with a strong base using methyl red as an indicator? What is the color change and the pH at the color change when a weak base is titrated with a strong acid using methyl red as an indicator? For which of these two types of titrations is methyl red a possible indicator?

67. Which of the indicators in Fig. 15.8 could be used for the titrations in Exercises 53 and 55?
68. Which of the indicators in Fig. 15.8 could be used for the titrations in Exercises 54 and 56?
69. Which of the indicators in Fig. 15.8 could be used for the titrations in Exercises 57 and 59?
70. Which of the indicators in Fig. 15.8 could be used for the titrations in Exercises 58 and 60?
71. Estimate the pH of a solution in which bromocresol green is blue and thymol blue is yellow. (See Fig. 15.8.)
72. A solution has a pH of 7.0. What would be the color of the solution if each of the following indicators were added? (See Fig. 15.8.)
- thymol blue
 - bromthymol blue
 - methyl red
 - crystal violet

Solubility Equilibria

73. Write balanced equations for the dissolution reactions and the corresponding solubility product expressions for each of the following solids.
- $\text{AgC}_2\text{H}_3\text{O}_2$
 - $\text{Al}(\text{OH})_3$
 - $\text{Ca}_3(\text{PO}_4)_2$
74. Write balanced equations for the dissolution reactions and the corresponding solubility product expressions for each of the following solids.
- Ag_2CO_3
 - $\text{Ce}(\text{IO}_3)_3$
 - BaF_2
75. Use the following data to calculate the K_{sp} value for each solid.
- The solubility of CaC_2O_4 is 4.8×10^{-5} mol/L.
 - The solubility of BiI_3 is 1.32×10^{-5} mol/L.

76. Use the following data to calculate the K_{sp} value for each solid.
- The solubility of $\text{Pb}_3(\text{PO}_4)_2$ is 6.2×10^{-12} mol/L.
 - The solubility of Li_2CO_3 is 7.4×10^{-2} mol/L.
77. The concentration of Pb^{2+} in a solution saturated with $\text{PbBr}_2(s)$ is 2.14×10^{-2} M. Calculate K_{sp} for PbBr_2 .
78. The concentration of Ag^+ in a solution saturated with $\text{Ag}_2\text{C}_2\text{O}_4(s)$ is 2.2×10^{-4} M. Calculate K_{sp} for $\text{Ag}_2\text{C}_2\text{O}_4$.
79. Calculate the solubility of each of the following compounds in moles per liter. Ignore any acid–base properties.
- Ag_3PO_4 , $K_{sp} = 1.8 \times 10^{-18}$
 - CaCO_3 , $K_{sp} = 8.7 \times 10^{-9}$
 - Hg_2Cl_2 , $K_{sp} = 1.1 \times 10^{-18}$ (Hg_2^{2+} is the cation in solution.)
80. Calculate the solubility of each of the following compounds in moles per liter. Ignore any acid–base properties.
- PbI_2 , $K_{sp} = 1.4 \times 10^{-8}$
 - CdCO_3 , $K_{sp} = 5.2 \times 10^{-12}$
 - $\text{Sr}_3(\text{PO}_4)_2$, $K_{sp} = 1 \times 10^{-31}$
81. Calculate the molar solubility of $\text{Co}(\text{OH})_3$, $K_{sp} = 2.5 \times 10^{-43}$.
82. Calculate the molar solubility of $\text{Mg}(\text{OH})_2$, $K_{sp} = 8.9 \times 10^{-12}$.
83. For each of the following pairs of solids, determine which solid has the smallest molar solubility.
- $\text{CaF}_2(s)$, $K_{sp} = 4.0 \times 10^{-11}$, or $\text{BaF}_2(s)$, $K_{sp} = 2.4 \times 10^{-5}$
 - $\text{Ca}_3(\text{PO}_4)_2(s)$, $K_{sp} = 1.3 \times 10^{-32}$, or $\text{FePO}_4(s)$, $K_{sp} = 1.0 \times 10^{-22}$
84. For each of the following pairs of solids, determine which solid has the smallest molar solubility.
- FeC_2O_4 , $K_{sp} = 2.1 \times 10^{-7}$, or $\text{Cu}(\text{IO}_4)_2$, $K_{sp} = 1.4 \times 10^{-7}$
 - Ag_2CO_3 , $K_{sp} = 8.1 \times 10^{-12}$, or $\text{Mn}(\text{OH})_2$, $K_{sp} = 2 \times 10^{-13}$
85. Calculate the solubility (in moles per liter) of $\text{Fe}(\text{OH})_3$ ($K_{sp} = 4 \times 10^{-38}$) in each of the following.
- water
 - a solution buffered at pH = 5.0
 - a solution buffered at pH = 11.0
86. The K_{sp} for silver sulfate (Ag_2SO_4) is 1.2×10^{-5} . Calculate the solubility of silver sulfate in each of the following.
- water
 - 0.10 M AgNO_3
 - 0.20 M K_2SO_4
87. Calculate the solubility of solid $\text{Ca}_3(\text{PO}_4)_2$ ($K_{sp} = 1.3 \times 10^{-32}$) in a 0.20 M Na_3PO_4 solution.
88. The solubility of $\text{Ce}(\text{IO}_3)_3$ in a 0.20 M KIO_3 solution is 4.4×10^{-8} mol/L. Calculate K_{sp} for $\text{Ce}(\text{IO}_3)_3$.
89. Which of the substances in Exercises 79 and 80 show increased solubility as the pH of the solution becomes more acidic? Write equations for the reactions that occur to increase the solubility.

90. For which salt in each of the following groups will the solubility depend on pH?
- AgF, AgCl, AgBr
 - Pb(OH)₂, PbCl₂
 - Sr(NO₃)₂, Sr(NO₂)₂
 - Ni(NO₃)₂, Ni(CN)₂
91. Will a precipitate form when 75.0 mL of 0.020 M BaCl₂ and 125 mL of 0.040 M Na₂SO₄ are mixed together?
92. Will a precipitate form when 100.0 mL of 4.0×10^{-4} M Mg(NO₃)₂ is added to 100.0 mL of 2.0×10^{-4} M NaOH?
93. Calculate the final concentrations of K⁺(aq), C₂O₄²⁻(aq), Ba²⁺(aq), and Br⁻(aq) in a solution prepared by adding 0.100 L of 0.200 M K₂C₂O₄ to 0.150 L of 0.250 M BaBr₂. (For BaC₂O₄, $K_{sp} = 2.3 \times 10^{-8}$.)
94. A solution is prepared by mixing 50.0 mL of 0.10 M Pb(NO₃)₂ with 50.0 mL of 1.0 M KCl. Calculate the concentrations of Pb²⁺ and Cl⁻ at equilibrium. K_{sp} for PbCl₂(s) is 1.6×10^{-5} .
95. A solution contains 1.0×10^{-5} M Na₃PO₄. What is the minimum concentration of AgNO₃ that would cause precipitation of solid Ag₃PO₄ ($K_{sp} = 1.8 \times 10^{-18}$)?
96. A solution contains 0.25 M Ni(NO₃)₂ and 0.25 M Cu(NO₃)₂. Can the metal ions be separated by slowly adding Na₂CO₃? Assume that for successful separation 99% of the metal ion must be precipitated before the other metal ion begins to precipitate, and assume no volume change on addition of Na₂CO₃.

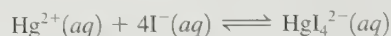
Complex Ion Equilibria

97. Write equations for the stepwise formation of each of the following complex ions.
- Co(NH₃)₆²⁺
 - Ag(NH₃)₂⁺
98. Write equations for the stepwise formation of each of the following complex ions.
- Ni(CN)₄²⁻
 - Mn(C₂O₄)₂²⁻
99. When aqueous KI is added gradually to mercury(II) nitrate, an orange precipitate forms. Continued addition of KI causes the precipitate to dissolve. Write balanced equations to explain these observations. (Hint: Hg²⁺ reacts with I⁻ to form HgI₄²⁻.)
100. As sodium chloride solution is added to a solution of silver nitrate, a white precipitate forms. Ammonia is added to the mixture and the precipitate dissolves. When potassium bromide solution is then added, a pale yellow precipitate appears. When a solution of sodium thiosulfate is added, the yellow precipitate dissolves. Finally, potassium iodide is added to the solution and a yellow precipitate forms. Write reactions for all the changes mentioned above. What conclusions can you draw concerning the sizes of the K_{sp} values for AgCl, AgBr, and AgI?

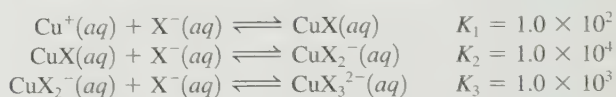
101. The overall formation constant for HgI₄²⁻ is 1.0×10^{30} . That is,

$$1.0 \times 10^{30} = \frac{[\text{HgI}_4^{2-}]}{[\text{Hg}^{2+}][\text{I}^-]^4}$$

What is the concentration of Hg²⁺ in 500.0 mL of a solution that was originally 0.010 M Hg²⁺ and 0.78 M I⁻? The reaction is



102. A solution is formed by mixing 50.0 mL of 10.0 M NaX with 50.0 mL of 2.0×10^{-3} M CuNO₃. Assume that Cu(I) forms complex ions with X⁻ as follows:



with an overall reaction

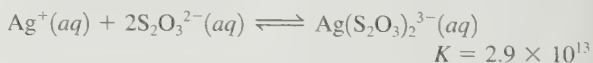


Calculate the following concentrations at equilibrium.

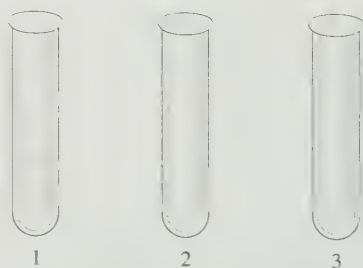
- CuX₃²⁻
- CuX₂⁻
- Cu⁺

103. a. Calculate the molar solubility of AgI in pure water. K_{sp} for AgI is 1.5×10^{-16} .
 b. Calculate the molar solubility of AgI in 3.0 M NH₃. The overall formation constant for Ag(NH₃)₂⁺ is 1.7×10^7 .
 c. Compare the calculated solubilities from parts a and b. Explain any differences.

104. Solutions of sodium thiosulfate are used to dissolve unexposed AgBr ($K_{sp} = 5.0 \times 10^{-13}$) in the developing process for black-and-white film. What mass of AgBr can dissolve in 1.00 L of 0.500 M Na₂S₂O₃? Ag⁺ reacts with S₂O₃²⁻ to form a complex ion:



105. A series of chemicals were added to some AgNO₃(aq). NaCl(aq) was added first to the silver nitrate solution with the end result shown below in test tube 1, NH₃(aq) was then added with the end result shown in test tube 2, and HNO₃(aq) was added last with the end result shown in test tube 3.

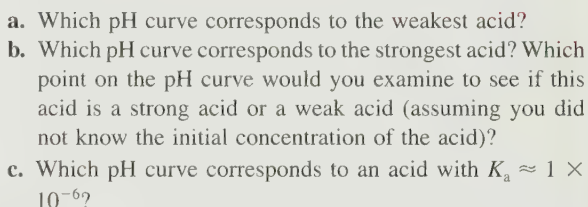


Explain the results shown in each test tube. Include a balanced equation for the reaction(s) taking place.

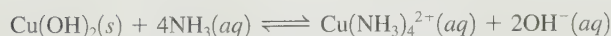
- a. $\text{HC}_2\text{H}_3\text{O}_2 + \text{OH}^- \rightleftharpoons \text{C}_2\text{H}_3\text{O}_2^- + \text{H}_2\text{O}$
 b. $\text{C}_2\text{H}_3\text{O}_2^- + \text{H}^+ \rightleftharpoons \text{HC}_2\text{H}_3\text{O}_2$
 c. $\text{HCl} + \text{NaOH} \rightleftharpoons \text{NaCl} + \text{H}_2\text{O}$

- ## Additional Exercises

- b. Calculate the pH after 20.0% (by moles) of the benzoic acid is converted to benzoate anion by addition of base. Use the dissociation equilibrium



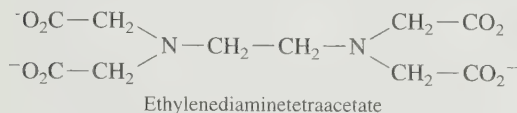
118. a. Using the K_{sp} value for $\text{Cu}(\text{OH})_2$ (1.6×10^{-19}) and the overall formation constant for $\text{Cu}(\text{NH}_3)_4^{2+}$ (1.0×10^{13}), calculate the value for the equilibrium constant for the following reaction:



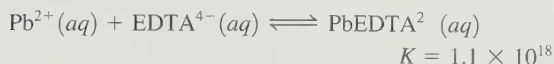
- b. Use the value of the equilibrium constant you calculated in part a to calculate the solubility (in mol/L) of $\text{Cu}(\text{OH})_2$ in 5.0 M NH_3 . In 5.0 M NH_3 the concentration of OH^- is 0.0095 M.
119. The K_{sp} of hydroxyapatite, $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, is 6.8×10^{-37} . Calculate the solubility of hydroxyapatite in pure water in moles per liter. How is the solubility of hydroxyapatite affected by adding acid? When hydroxyapatite is treated with fluoride, the mineral fluorapatite, $\text{Ca}_5(\text{PO}_4)_3\text{F}$, forms. The K_{sp} of this substance is 1×10^{-60} . Calculate the solubility of fluorapatite in water. How do these calculations provide a rationale for the fluoridation of drinking water?
120. In the chapter discussion of precipitate formation, we ran the precipitation reaction to completion and then let some of the precipitate redissolve to get back to equilibrium. To see why, redo Sample Exercise 15.17, where

Initial Concentration (mol/L)	Equilibrium Concentration (mol/L)
$[\text{Mg}^{2+}]_0 = 3.75 \times 10^{-3}$	
$[\text{F}^-]_0 = 6.25 \times 10^{-2}$	
$\xrightarrow[\text{reacts to form MgF}_2]{x \text{ mol/Mg}^{2+}}$	$[\text{Mg}^{2+}] = 3.75 \times 10^{-3} - x$ $[\text{F}^-] = 6.25 \times 10^{-2} - 2x$

121. Calculate the concentration of Pb^{2+} in each of the following.
- a saturated solution of $\text{Pb}(\text{OH})_2$, $K_{\text{sp}} = 1.2 \times 10^{-15}$
 - a saturated solution of $\text{Pb}(\text{OH})_2$ buffered at pH = 13.00
 - Ethylenediaminetetraacetate (EDTA^{4-}) is used as a complexing agent in chemical analysis and has the following structure:



Solutions of EDTA^{4-} are used to treat heavy metal poisoning by removing the heavy metal in the form of a soluble complex ion. The complex ion virtually eliminates the heavy metal ions from reacting with biochemical systems. The reaction of EDTA^{4-} with Pb^{2+} is



Consider a solution with 0.010 mol $\text{Pb}(\text{NO}_3)_2$ added to 1.0 L of an aqueous solution buffered at pH = 13.00 and containing 0.050 M Na_4EDTA . Does $\text{Pb}(\text{OH})_2$ precipitate from this solution?

Challenge Problems

122. Another way to treat data from a pH titration is to graph the absolute value of the change in pH per change in milliliters

added versus milliliters added ($\Delta\text{pH}/\Delta\text{mL}$ versus mL added). Make this graph using your results from Exercise 57. What advantage might this method have over the traditional method for treating titration data?

123. A buffer is made using 45.0 mL of 0.750 M $\text{HC}_3\text{H}_5\text{O}_2$ ($K_a = 1.3 \times 10^{-5}$) and 55.0 mL of 0.700 M $\text{NaC}_3\text{H}_5\text{O}_2$. What volume of 0.10 M NaOH must be added to change the pH of the original buffer solution by 2.5%?
124. A 0.400 M solution of ammonia was titrated with hydrochloric acid to the equivalence point, where the total volume was 1.50 times the original volume. At what pH does the equivalence point occur?
125. What volume of 0.0100 M NaOH must be added to 1.00 L of 0.0500 M HOCl to achieve a pH of 8.00?
126. Consider a solution formed by mixing 50.0 mL of 0.100 M H_2SO_4 , 30.0 mL of 0.100 M HOCl , 25.0 mL of 0.200 M NaOH, 25.0 mL of 0.100 M $\text{Ba}(\text{OH})_2$, and 10.0 mL of 0.150 M KOH. Calculate the pH of this solution.
127. When a diprotic acid, H_2A , is titrated by NaOH, the protons on the diprotic acid are generally removed one at a time, resulting in a pH curve that has the following generic shape:



- a. Notice that the plot has essentially two titration curves. If the first equivalence point occurs at 100.0 mL of NaOH added, what volume of NaOH added corresponds to the second equivalence point?
- b. For the following volumes of NaOH added, list the major species present after the OH^- reacts completely.
- 0 mL NaOH added
 - between 0 and 100.0 mL NaOH added
 - 100.0 mL NaOH added
 - between 100.0 and 200.0 mL NaOH added
 - 200.0 mL NaOH added
 - after 200.0 mL NaOH added
- c. If the pH at 50.0 mL of NaOH added is 4.0 and the pH at 150.0 mL of NaOH added is 8.0, determine the values K_{a1} and K_{a2} for the diprotic acid.
128. A few drops of each of the indicators shown in the accompanying table were placed in separate portions of a 1.0 M solution of a weak acid, HX. The results are shown in the last column of the table. What is the approximate pH of the solution containing HX? Calculate the approximate value of K_a for HX.

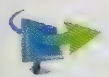
Indicator	Color of HIn	Color of In ⁻	pK _a of HIn	HX
Bromphenol blue	Yellow	Blue	4.0	Blue
Bromcresol purple	Yellow	Purple	6.0	Yellow
Bromcresol green	Yellow	Blue	4.8	Green
Alizarin	Yellow	Red	6.5	Yellow

129. a. Calculate the molar solubility of SrF₂ in water, ignoring the basic properties of F⁻. (For SrF₂, $K_{sp} = 7.9 \times 10^{-10}$.)
 b. Would the measured molar solubility of SrF₂ be greater than or less than the value calculated in part a? Explain.
 c. Calculate the molar solubility of SrF₂ in a solution buffered at pH = 2.00. (K_a for HF is 7.2×10^{-4} .)
130. A solution saturated with a salt of the type M₃X₂ has an osmotic pressure of 2.64×10^{-2} atm at 25°C. Calculate the K_{sp} value for the salt, assuming ideal behavior.

Marathon Problem*

This problem is designed to incorporate several concepts and techniques into one situation. Marathon Problems can be used in class by groups of students to help facilitate problem-solving skills.

131. A 225-mg sample of a diprotic acid is dissolved in enough water to make 250. mL of solution. The pH of this solution is 2.06. A saturated solution of calcium hydroxide ($K_{sp} = 1.3 \times 10^{-6}$) is prepared by adding excess calcium hydroxide to pure water and then removing the undissolved solid by filtration. Enough of the calcium hydroxide solution is added to the solution of the acid to reach the second equivalence point. The pH at the second equivalence point (as determined by a pH meter) is 7.96. The first dissociation constant for the acid (K_{a1}) is 5.90×10^{-2} . Assume that the volumes of the solutions are additive, all solutions are at 25°C, and that K_{a1} is at least 1000 times greater than K_{a2} .
- a. Calculate the molar mass of the acid.
 b. Calculate the second dissociation constant for the acid (K_{a2}).



Media Activities

1. a. Open the Buffers Understanding Concepts activity on the student CD. In the example, when 0.10 mol of HCl is added to the 1.0 M HF/1.0 M F⁻ buffer, the pH changes from 3.16 to 3.07. How does this illustrate a primary property of buffers? What would happen to the concentrations of 1.0 M

HF and 1.0 M F⁻ if 0.10 mol of NaOH were added instead? Calculate the pH of the resulting solution. In general, best buffers have a pH value close to the pK_a value of the weak acid component ($pH = pK_a$ for best buffer). Using the Henderson-Hasselbalch equation, how are the weak acid concentration and the conjugate base concentration related for a best buffer?

- b. Under More Examples, HCl is added in 0.20-mol increments to pure water and to a 1.0 M HF/1.0 M NaF buffer. Notice the slow change in pH of the buffer as compared to the change in pH of water as HCl is added. This exemplifies the primary property of buffers as solutions that resist pH change. One thing you should be able to do is to calculate the pH as 0.20-mol increments are added. To practice, check that the pH values given are correct. (Hint: For the buffer, added H⁺ from the HCl can be assumed to react completely with F⁻ to form HF. Perform this stoichiometry problem first to determine the equilibrium concentrations of HF and F⁻ in the buffer, then do the buffer problem.)
2. a. Open the Neutralization of a Strong Acid by a Strong Base Visualization on the student CD, which illustrates what happens during the titration of a strong acid by a strong base. When HCl is added to water, what happens? Is the solution acidic, basic, or neutral? As NaOH is added to the solution containing the HCl, what happens?
- b. Let's assume that three molecules of HCl are present initially. If two molecules of NaOH are added, what would be present in solution initially before any reaction? What would be present after the OH⁻ reacts completely with the H⁺? Is the solution acidic, basic, or neutral? If 3 molecules of NaOH are added, would the solution be acidic, basic, or neutral? This is called the equivalence point and is represented in the animation. What is meant by the equivalence point? When five molecules of NaOH have been added, is the solution acidic, basic, or neutral? Explain in terms of major species present after the OH⁻ neutralizes (reacts) with the H⁺ present initially.
- c. With the above discussion in mind, do Exercises 15.53 and 15.54 in the text, which illustrate strong acid/strong base titration problems. For each problem, sketch the pH curve and then compare and contrast the two curves. Make sure that you understand why the pH values are acidic, basic, or neutral at the various volumes of titrant added. The key is realizing whether you have excess H⁺ from the strong acid, excess OH⁻ from the strong base, or equal amounts of H⁺ and OH⁻ (the equivalence point).
3. a. Review Table 15.4 in the text, which lists K_{sp} values for various salts (ionic compounds). The K_{sp} values listed refer to a specific reaction. What is this reaction? Look at the fluoride salts. Which salt is most soluble in water? Least soluble in water? The K_{sp} values for AgCl is larger than the K_{sp} value for CaF₂, yet CaF₂ is more soluble in water than AgCl. Why is this? Calculate the molar solubility of each of these salts. Explain the terms *saturated* and *supersaturated*. View the Supersaturated Sodium Acetate Visualization on the student CD to learn about supersaturated solutions.

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Spontaneity, Entropy, and Free Energy

The first law of thermodynamics is a statement of the law of conservation of energy: Energy can be neither created nor destroyed. In other words, *the energy of the universe is constant*. Although the total energy is constant, the various forms of energy can be interchanged in physical and chemical processes. For example, if you drop a book, some of the initial potential energy of the book is changed to kinetic energy, which is then transferred to the atoms in the air and the floor as random motion. The net effect of this process is to change a given quantity of potential energy to exactly the same quantity of thermal energy. Energy has been converted from one form to another, but the same quantity of energy exists before and after the process.

Now let's consider a chemical example. When methane is burned in excess oxygen, the major reaction is



This reaction produces a quantity of energy, which is released as heat. This energy flow results from the lowering of the potential energy stored in the bonds of CH_4 and O_2 as they react to form CO_2 and H_2O . This is illustrated in Fig. 16.1. Potential energy has been converted to thermal energy, but the energy content of the universe has remained constant in accordance with the first law of thermodynamics.



Solid carbon dioxide (dry ice), when placed in water, causes violent bubbling as gaseous CO_2 is released. The “fog” is moisture condensed from the cold air.

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- 16.1 Spontaneous Processes and Entropy
- 16.2 Entropy and the Second Law of Thermodynamics
- 16.3 The Effect of Temperature on Spontaneity
- 16.4 Free Energy
- 16.5 Entropy Changes in Chemical Reactions
- 16.6 Free Energy and Chemical Reactions
- 16.7 The Dependence of Free Energy on Pressure
 - The Meaning of ΔG for a Chemical Reaction
- 16.8 Free Energy and Equilibrium
 - The Temperature Dependence of K
- 16.9 Free Energy and Work

FIGURE 16.1

When methane and oxygen react to form carbon dioxide and water, the products have lower potential energy than the reactants. This change in potential energy results in energy flow (heat) to the surroundings.

The first law of thermodynamics is used mainly for energy bookkeeping, that is, to answer such questions as

How much energy is involved in the change?

Does energy flow into or out of the system?

What form does the energy finally assume?

The first law of thermodynamics: The energy of the universe is constant.

Although the first law of thermodynamics provides the means for accounting for energy, it gives no hint as to why a particular process occurs in a given direction. This is the main question to be considered in this chapter.

16.1 Spontaneous Processes and Entropy

Spontaneous does not mean fast.

A process is said to be *spontaneous* if it occurs without outside intervention. **Spontaneous processes** may be fast or slow. As we will see in this chapter, thermodynamics can tell us the *direction* in which a process will occur but can say nothing about the *speed* of the process. As we saw in Chapter 12, the rate of a reaction depends on many factors, such as activation energy, temperature, concentration, and catalysts, and we were able to explain these effects using a simple collision model. In describing a chemical reaction, the discipline of chemical kinetics focuses on the pathway between reactants and products; thermodynamics considers only the initial and final states and does not require knowledge of the pathway between reactants and products (see Fig. 16.2).

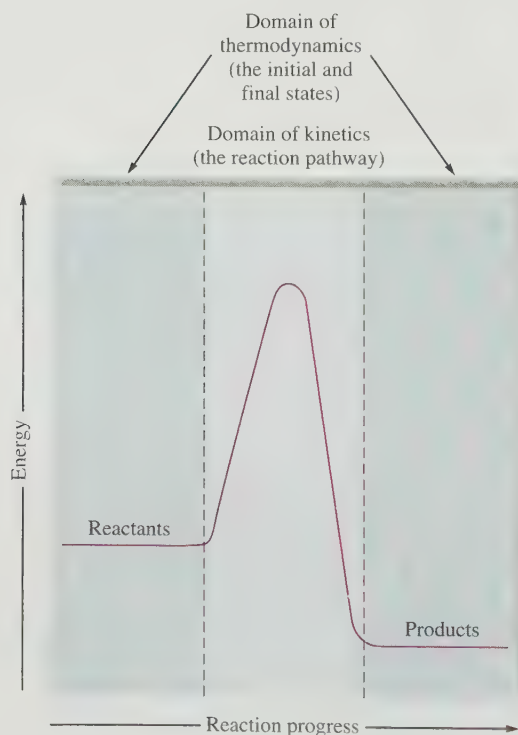


FIGURE 16.2

The rate of a reaction depends on the pathway from reactants to products; this is the domain of kinetics. Thermodynamics tells us whether a reaction is spontaneous based only on the properties of the reactants and products. The predictions of thermodynamics do not require knowledge of the pathway between reactants and products.

In summary, thermodynamics lets us predict whether a process will occur but gives no information about the amount of time required for the process. For example, according to the principles of thermodynamics, a diamond should change spontaneously to graphite. The fact that we do not observe this process does not mean the prediction is wrong; it simply means the process is very slow. Thus we need both thermodynamics and kinetics to describe reactions fully.

To explore the idea of spontaneity, consider the following physical and chemical processes:

A ball rolls down a hill but never spontaneously rolls back up the hill.

If exposed to air and moisture, steel rusts spontaneously. However, the iron oxide in rust does not spontaneously change back to iron metal and oxygen gas.

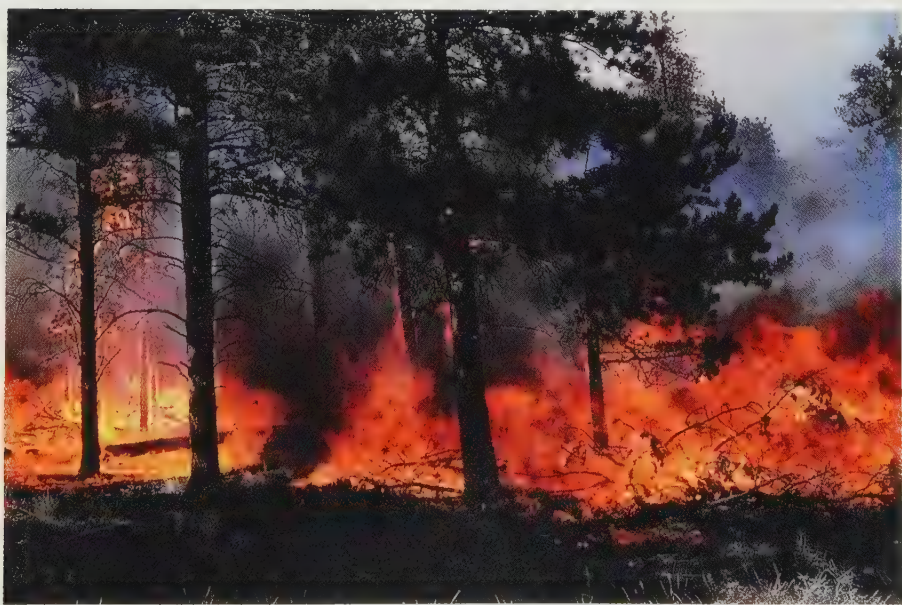
A gas fills its container uniformly. It never spontaneously collects at one end of the container.

Heat flow always occurs from a hot object to a cooler one. The reverse process never occurs spontaneously.

Wood burns spontaneously in an exothermic reaction to form carbon dioxide and water, but wood is not formed when carbon dioxide and water are heated together.

At temperatures below 0°C , water spontaneously freezes, and at temperatures above 0°C , ice spontaneously melts.

What thermodynamic principle will provide an explanation of why, under a given set of conditions, each of these diverse processes occurs in one direction and never in the reverse? In searching for an answer, we could explain the behavior of a ball on a hill in terms of gravity. But what does gravity have to do with the rusting of a nail or the freezing of water? Early developers of thermodynamics thought that exothermicity might be the key—that a process would be spontaneous if it were exothermic. Although this factor does appear to be important, since many



Plant materials burn to form carbon dioxide and water.



A disordered pile of playing cards.

Probability refers to likelihood.

spontaneous processes are exothermic, it is not the total answer. For example, the melting of ice, which occurs spontaneously at temperatures greater than 0°C , is an endothermic process.

What common characteristic causes the processes listed above to be spontaneous in one direction only? After many years of observation, scientists have concluded that the characteristic common to all spontaneous processes is an increase in a property called **entropy**, denoted by the symbol S . *The driving force for a spontaneous process is an increase in the entropy of the universe.*

What is entropy? Although there is no simple definition that is completely accurate, *entropy can be viewed as a measure of molecular randomness or disorder.* The natural progression of things is from order to disorder, from lower entropy to higher entropy. To illustrate the natural tendency toward disorder, you only have to think about the condition of your room. Your room naturally tends to get messy (disordered), because an ordered room requires everything to be in its place. There are simply many more ways for things to be out of place than for them to be in their places.

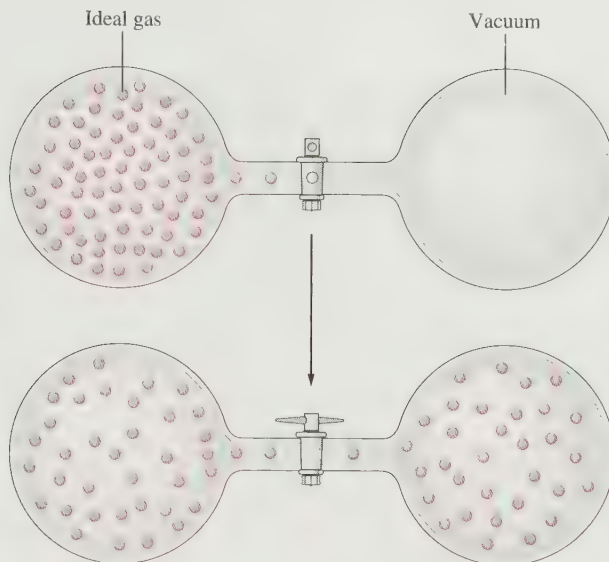
As another example, suppose you have a deck of playing cards ordered in some particular way. You throw these cards into the air and pick them all up at random. Looking at the new sequence of the cards, you would be very surprised to find that it matched the original order. Such an event would be possible, but *very improbable*. There are billions of ways for the deck to be disordered, but only one way to be ordered according to your definition. Thus the chances of picking the cards up out of order are much greater than the chance of picking them up in order. It is natural for disorder to increase.

Entropy is a thermodynamic function that describes the *number of arrangements* (positions and/or energy levels) that are *available to a system* existing in a given state. Entropy is closely associated with probability. The key concept is that the more ways a particular state can be achieved, the greater is the likelihood (probability) of finding that state. In other words, *nature spontaneously proceeds toward the states that have the highest probabilities of existing.* This conclusion is not surprising at all. The difficulty comes in connecting this concept to real-life processes. For example, what does the spontaneous rusting of steel have to do with probability? Understanding the connection between entropy and spontaneity will allow us to answer such questions. We will begin to explore this connection by considering a very simple process, the expansion of an ideal gas into a vacuum, as represented in Fig. 16.3. Why is this process spontaneous? The driving force is probability. Because there are more ways of having the gas evenly spread throughout the container than there are ways for it to be in any other possible state, the gas spontaneously attains the uniform distribution.

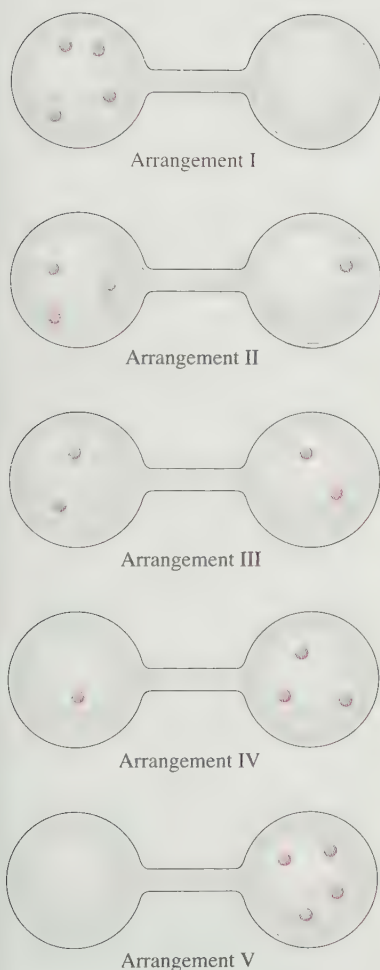
To understand this conclusion, we will greatly simplify the system and consider the possible arrangements of only four gas molecules in the two-bulbed container (Fig. 16.4). How many ways can each arrangement (state) be achieved? Arrangements I and V can be achieved in only one way—all the molecules must be in one end. Arrangements II and V can be achieved in four ways, as shown in Table 16.1. Each configuration that gives a particular arrangement is called a *microstate*. Arrangement I has one microstate, and arrangement II has four microstates. Arrangement III can be achieved in six ways (six microstates), as shown in Table 16.1. *Which arrangement is most likely to occur?* The one that can be achieved in the greatest number of ways. Thus arrangement III is most probable. The relative probabilities of arrangements III, II, and I are 6 : 4 : 1. We have discovered an important principle: The probability of occurrence of a particular arrangement (state) depends on the number of ways (microstates) in which that arrangement can be achieved.

FIGURE 16.3

The expansion of an ideal gas into an evacuated bulb.



The consequences of this principle are dramatic for large numbers of molecules. One gas molecule in the flask in Fig. 16.4 has one chance in two of being in the left bulb. We say that the probability of finding the molecule in the left bulb is $\frac{1}{2}$.

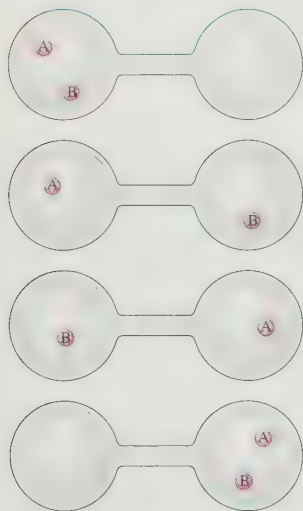
**FIGURE 16.4**

Possible arrangements (states) of four molecules in a two-bulbed flask.

TABLE 16.1 The Microstates That Give a Particular Arrangement (State)

Arrangement	Microstates	
I		
II		
III		
IV		
V		

For two molecules in the flask, there are four possible microstates:



Thus there is one chance in four of finding

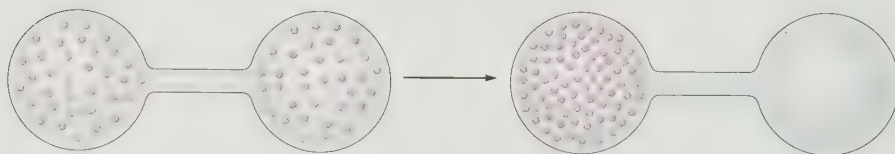


TABLE 16.2 Probability of Finding All the Molecules in the Left Bulb as a Function of the Total Number of Molecules

Number of Molecules	Relative Probability of Finding All Molecules in the Left Bulb
1	$\frac{1}{2}$
2	$\frac{1}{2} \times \frac{1}{2} = \frac{1}{2^2} = \frac{1}{4}$
3	$\frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} = \frac{1}{2^3} = \frac{1}{8}$
5	$\frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} = \frac{1}{2^5} = \frac{1}{32}$
10	$\frac{1}{2^{10}} = \frac{1}{1024}$
n	$\frac{1}{2^n} = \left(\frac{1}{2}\right)^n$
6×10^{23} (1 mole)	$\left(\frac{1}{2}\right)^{6 \times 10^{23}} \approx 10^{-(2 \times 10^{23})}$

For two molecules in the flask, there is one chance in two of finding each molecule in the left bulb, so there is one chance in four ($\frac{1}{2} \times \frac{1}{2} = \frac{1}{4}$) that *both* molecules will be in the left bulb. As the number of molecules increases, the relative probability of finding all of them in the left bulb decreases, as shown in Table 16.2. For 1 mole of gas, the probability of finding all the molecules in the left bulb is so small that this arrangement would “never” occur.

Thus a gas placed in one end of a container will spontaneously expand to fill the entire vessel evenly because, for a large number of gas molecules, there is a huge number of microstates in which equal numbers of molecules are in both ends. On the other hand, the opposite process,



although not impossible, is *highly* improbable, since only one microstate leads to this arrangement. Therefore, this process does not occur spontaneously.

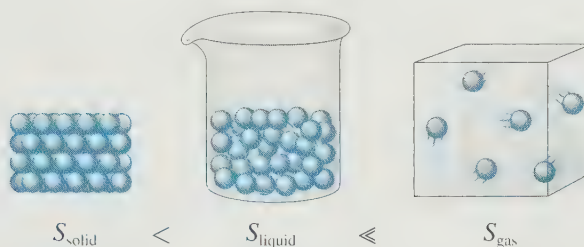
The type of probability we have been considering in this example is called **positional probability** because it depends on the number of configurations in space (positional microstates) that yield a particular state. A gas expands into a vacuum to give a uniform distribution because the expanded state has the highest positional probability, that is, the largest entropy, of the states available to the system.

Positional probability is also illustrated by changes of state. In general, positional entropy increases in going from solid to liquid to gas. A mole of a substance

Solid, liquid, and gaseous states were compared in Chapter 10.

Solids are more ordered than liquids or gases and thus have lower entropy.

has a much smaller volume in the solid state than it does in the gaseous state. In the solid state, the molecules are close together, with relatively few positions available to them; in the gaseous state, the molecules are far apart, with many more positions available to them. The liquid state is closer to the solid state than it is to the gaseous state in these terms. We can summarize these comparisons as follows:



The tendency to mix is due to the increased volume available to the particles of each component of the mixture. For example, when two liquids are mixed, the molecules of each liquid have more available volume and thus more available positions.

Positional entropy is also very important in the formation of solutions. In Chapter 11 we saw that solution formation is favored by the natural tendency for substances to mix. We can now be more precise. The entropy change associated with the mixing of two pure substances is expected to be positive. An increase in entropy is expected because there are many more microstates for the mixed condition than for the separated condition. This effect is due principally to the increased volume available to a given “particle” after mixing occurs. For example, when two liquids are mixed to form a solution, the molecules of each liquid have more available volume and thus more available positions. Therefore, the increase in positional entropy associated with mixing favors the formation of solutions.

SAMPLE EXERCISE 16.1

Positional Entropy

For each of the following pairs, choose the substance with the higher positional entropy (per mole) at a given temperature.

- Solid CO_2 and gaseous CO_2
- N_2 gas at 1 atm and N_2 gas at 1.0×10^{-2} atm

SOLUTION

- Since a mole of gaseous CO_2 has the greater volume by far, the molecules have many more available positions than in a mole of solid CO_2 . Thus gaseous CO_2 has the higher positional entropy.
- A mole of N_2 gas at 1×10^{-2} atm has a volume 100 times that (at a given temperature) of a mole of N_2 gas at 1 atm. Thus N_2 gas at 1×10^{-2} atm has the higher positional entropy.

See Exercise 16.19.

SAMPLE EXERCISE 16.2

Predicting Entropy Changes

Predict the sign of the entropy change for each of the following processes.

- Solid sugar is added to water to form a solution.
- Iodine vapor condenses on a cold surface to form crystals.

SOLUTION

- The sugar molecules become randomly dispersed in the water when the solution forms and thus have access to a larger volume and a larger number of possible positions. The positional disorder is increased, and there will be an increase in entropy. ΔS is positive, since the final state has a larger entropy than the initial state, and $\Delta S = S_{\text{final}} - S_{\text{initial}}$.
- Gaseous iodine is forming a solid. This process involves a change from a relatively large volume to a much smaller volume, which results in lower positional disorder. For this process ΔS is negative (the entropy decreases).

See Exercise 16.20.

16.2 Entropy and the Second Law of Thermodynamics

The total energy of the universe is constant, but the entropy is increasing.

We have seen that processes are spontaneous when they result in an increase in disorder. Nature always moves toward the most probable state available to it. We can state this principle in terms of entropy: *In any spontaneous process there is always an increase in the entropy of the universe.* This is the **second law of thermodynamics**. Contrast this with the first law of thermodynamics, which tells us that the energy of the universe is constant. Energy is conserved in the universe, but entropy is not. In fact, the second law can be paraphrased as follows: *The entropy of the universe is increasing.*

As in Chapter 6, we find it convenient to divide the universe into a system and the surroundings. Thus we can represent the change in the entropy of the universe as

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

where ΔS_{sys} and ΔS_{surr} represent the changes in entropy that occur in the system and surroundings, respectively.

To predict whether a given process will be spontaneous, we must know the sign of ΔS_{univ} . If ΔS_{univ} is positive, the entropy of the universe increases, and the process is spontaneous in the direction written. If ΔS_{univ} is negative, the process is spontaneous in the *opposite* direction. If ΔS_{univ} is zero, the process has no tendency to occur, and the system is at equilibrium. To predict whether a process is spontaneous, we must consider the entropy changes that occur both in the system and in the surroundings and then take their sum.

SAMPLE EXERCISE 16.3

The Second Law

In a living cell, large molecules are assembled from simple ones. Is this process consistent with the second law of thermodynamics?

SOLUTION

To reconcile the operation of an order-producing cell with the second law of thermodynamics, we must remember that ΔS_{univ} , not ΔS_{sys} , must be positive for a process to be spontaneous. A process for which ΔS_{sys} is negative can be spontaneous if the associated ΔS_{surr} is both larger and positive. The operation of a cell is such a process.

See Questions 16.9 and 16.11.

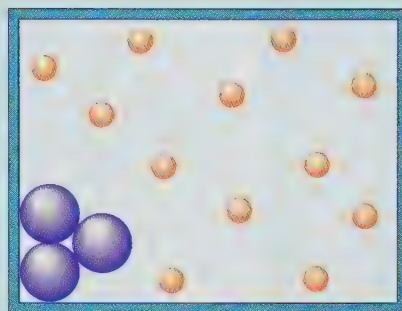
CHEMICAL IMPACT

Entropy: An Organizing Force?

In this text we have emphasized the meaning of the second law of thermodynamics—that the entropy of the universe is always increasing. Although the results of all our experiments support this conclusion, this does not mean that order cannot appear spontaneously in a given part of the universe. The best example of this phenomenon involves the assembly of cells in living organisms. Of course, when a process that creates an ordered system is examined in detail, it is found that other parts of the process involve an increase in disorder such that the sum of all the entropy changes is positive. In fact, scientists are now finding that the search for maximum entropy in one part of a system can be a powerful force for organization in another part of the system.

To understand how entropy can be an organizing force, look at the accompanying figure. In a system containing large and small “balls” as shown in the figure, the small balls can “herd” the large balls into clumps in the corners and near the walls. This clears out the maximum space for the small balls so that they can move more freely, thus maximizing the entropy of the system, as demanded by the second law of thermodynamics.

In essence, the ability to maximize entropy by sorting different-sized objects creates a kind of attractive force, called a *depletion*, or *excluded-volume, force*. These “entropic forces” operate for objects in the size range of approximately 10^{-8} to approximately 10^{-6} m. For entropy-induced ordering to occur, the particles must be constantly jostling each other and must be constantly agitated by solvent molecules, thus making gravity unimportant.



There is increasing evidence that entropic ordering is important in many biological systems. For example, this phenomenon seems to be responsible for the clumping of sickle-cell hemoglobin in the presence of much smaller proteins that act as the “smaller balls.” Entropic forces also have been linked to the clustering of DNA in cells without nuclei, and Allen Minton of the National Institutes of Health in Bethesda, Maryland, is studying the role of entropic forces in the binding of proteins to cell membranes.

Entropic ordering also appears in nonbiological settings, especially in the ways polymer molecules clump together. For example, polymers added to paint to improve the flow characteristics of the paint actually caused it to coagulate because of depletion forces.

Thus, as you probably have concluded already, entropy is a complex issue. As entropy drives the universe to its ultimate death of maximum chaos, it provides some order along the way.

16.3 The Effect of Temperature on Spontaneity

To explore the interplay of ΔS_{sys} and ΔS_{surr} in determining the sign of ΔS_{univ} , we will first discuss the change of state for one mole of water from liquid to gas,



considering the water to be the system and everything else the surroundings.

What happens to the entropy of water in this process? A mole of liquid water (18 grams) has a volume of approximately 18 mL. A mole of gaseous water at 1 atmosphere and 100°C occupies a volume of approximately 31 liters. Clearly, there are many more positions available to the water molecules in a volume of 31 L than in 18 mL, and the vaporization of water is favored by this increase in positional probability. That is, for this process the entropy of the system increases; ΔS_{sys} has a positive sign.



Boiling water to form steam increases its volume and thus its entropy.

In an endothermic process, heat flows from the surroundings into the system. In an exothermic process, heat flows into the surroundings from the system.

What about the entropy change in the surroundings? Although we will not prove it here, entropy changes in the surroundings are determined primarily by the flow of energy into or out of the system as heat. To understand this, suppose an exothermic process transfers 50 J of energy as heat to the surroundings, where it becomes thermal energy, that is, kinetic energy associated with the random motions of atoms. Thus this flow of energy into the surroundings increases the random motions of atoms there and thereby increases the entropy of the surroundings. The sign of ΔS_{surr} is positive. When an endothermic process occurs in the system, it produces the opposite effect. Heat flows from the surroundings to the system, and the random motions of the atoms in the surroundings decrease, decreasing the entropy of the surroundings. The vaporization of water is an endothermic process. Thus, for this change of state, ΔS_{surr} is negative.

Remember it is the sign of ΔS_{univ} that tells us whether the vaporization of water is spontaneous. We have seen that ΔS_{sys} is positive and favors the process and that ΔS_{surr} is negative and unfavorable. Thus the components of ΔS_{univ} are in opposition. Which one controls the situation? The answer *depends on the temperature*. We know that at a pressure of 1 atmosphere, water changes spontaneously from liquid to gas at all temperatures above 100°C. Below 100°C, the opposite process (condensation) is spontaneous.

Since ΔS_{sys} and ΔS_{surr} are in opposition for the vaporization of water, the temperature must have an effect on the relative importance of these two terms. To understand why this is so, we must discuss in more detail the factors that control the entropy changes in the surroundings. The central idea is that *the entropy changes in the surroundings are primarily determined by heat flow*. An exothermic process in the system increases the entropy of the surroundings, because the resulting energy flow increases the random motions in the surroundings. This means that exothermicity is an important driving force for spontaneity. In earlier chapters we have seen that a system tends to undergo changes that lower its energy. We now understand the reason for this tendency. When a system at constant temperature moves to a lower energy, the energy it gives up is transferred to the surroundings, leading to an increase in entropy there.

The significance of exothermicity as a driving force *depends on the temperature at which the process occurs*. That is, the magnitude of ΔS_{surr} depends on the temperature at which the heat is transferred. We will not attempt to prove this fact here. Instead, we offer an analogy. Suppose that you have \$50 to give away. Giving it to a millionaire would not create much of an impression—a millionaire has money to spare. However, to a poor college student, \$50 would represent a significant sum and would be received with considerable joy. The same principle can be applied to energy transfer via the flow of heat. If 50 J of energy is transferred to the surroundings, the impact of that event depends greatly on the temperature. If the temperature of the surroundings is very high, the atoms there are in rapid motion. The 50 J of energy will not make a large percent change in these motions. On the other hand, if 50 J of energy is transferred to the surroundings at a very low temperature, where atomic motion is slow, the energy will cause a large percent change in these motions. *The impact of the transfer of a given quantity of energy as heat to or from the surroundings will be greater at lower temperatures.*

For our purposes, there are two important characteristics of the entropy changes that occur in the surroundings:

1. The sign ΔS_{surr} depends on the direction of the heat flow. At constant temperature, an exothermic process in the system causes heat to flow into the surroundings,

In a process occurring at constant temperature, the tendency for the system to lower its energy results from the positive value of ΔS_{surr} .

increasing the random motions and thus the entropy of the surroundings. For this case, ΔS_{surr} is positive. The opposite is true for an endothermic process in a system at constant temperature. Note that although the driving force described here really results from the change in entropy, it is often described in terms of energy: Nature tends to seek the lowest possible energy.

2. *The magnitude of ΔS_{surr} depends on the temperature.* The transfer of a given quantity of energy as heat produces a much greater percent change in the randomness of the surroundings at a low temperature than it does at a high temperature. Thus ΔS_{surr} depends directly on the quantity of heat transferred and inversely on temperature. In other words, the tendency for the system to lower its energy becomes a more important driving force at lower temperatures.

$$\begin{array}{l} \text{Driving force} \\ \text{provided by} \\ \text{the energy flow} \\ \text{(heat)} \end{array} = \begin{array}{l} \text{magnitude of the} \\ \text{entropy change of} \\ \text{the surroundings} \end{array} = \frac{\text{quantity of heat (J)}}{\text{temperature (K)}}$$

These ideas are summarized as follows:

Exothermic process:
 $\Delta S_{\text{surr}} = \text{positive}$

$$\text{Exothermic process: } \Delta S_{\text{surr}} = + \frac{\text{quantity of heat (J)}}{\text{temperature (K)}}$$

Endothermic process:
 $\Delta S_{\text{surr}} = \text{negative}$

$$\text{Endothermic process: } \Delta S_{\text{surr}} = - \frac{\text{quantity of heat (J)}}{\text{temperature (K)}}$$

We can express ΔS_{surr} in terms of the change in enthalpy ΔH for a process occurring at constant pressure, since

$$\text{Heat flow (constant } P) = \text{change in enthalpy} = \Delta H$$

When no subscript is present, the quantity (for example, ΔH) refers to the system.

Recall that ΔH consists of two parts: a sign and a number. The *sign* indicates the direction of flow, where a plus sign means into the system (endothermic) and a minus sign means out of the system (exothermic). The *number* indicates the quantity of energy.

Combining all these concepts produces the following definition of ΔS_{surr} for a reaction that takes place under conditions of constant temperature (in Kelvins) and pressure:

$$\Delta S_{\text{surr}} = - \frac{\Delta H}{T}$$

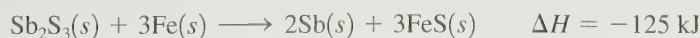
The minus sign changes the point of view from the system to the surroundings.

The minus sign is necessary because the sign of ΔH is determined with respect to the reaction system, and this equation expresses a property of the surroundings. This means that if the reaction is exothermic, ΔH has a negative sign, but since heat flows into the surroundings, ΔS_{surr} is positive.

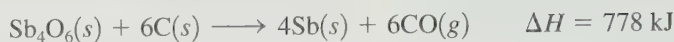
SAMPLE EXERCISE 16.4

Determining ΔS_{surr}

In the metallurgy of antimony, the pure metal is recovered via different reactions, depending on the composition of the ore. For example, iron is used to reduce antimony in sulfide ores:



Carbon is used as the reducing agent for oxide ores:



Calculate ΔS_{surr} for each of these reactions at 25°C and 1 atm.

SOLUTION

We use

$$\Delta S_{\text{surr}} = -\frac{\Delta H}{T}$$

where

$$T = 25 + 273 = 298 \text{ K}$$

For the sulfide ore reaction,

$$\Delta S_{\text{surr}} = -\frac{-125 \text{ kJ}}{298 \text{ K}} = 0.419 \text{ kJ/K} = 419 \text{ J/K}$$

Note that ΔS_{surr} is positive, as it should be, since this reaction is exothermic and heat flow occurs to the surroundings, increasing the randomness of the surroundings.

For the oxide ore reaction,

$$\Delta S_{\text{surr}} = -\frac{778 \text{ kJ}}{298} = -2.61 \text{ kJ/K} = -2.61 \times 10^3 \text{ J/K}$$

In this case ΔS_{surr} is negative because heat flow occurs from the surroundings to the system.

See Exercises 16.21 and 16.22.

We have seen that the spontaneity of a process is determined by the entropy change it produces in the universe. We also have seen that ΔS_{univ} has two components, ΔS_{sys} and ΔS_{surr} . If for some process both ΔS_{sys} and ΔS_{surr} are positive, then ΔS_{univ} is positive, and the process is spontaneous. If, on the other hand, both ΔS_{sys} and ΔS_{surr} are negative, the process does not occur in the direction indicated but is spontaneous in the opposite direction. Finally, if ΔS_{sys} and ΔS_{surr} have opposite signs, the spontaneity of the process depends on the sizes of the opposing terms. These cases are summarized in Table 16.3.

TABLE 16.3 Interplay of ΔS_{sys} and ΔS_{surr} in Determining the Sign of ΔS_{univ}

Signs of Entropy Changes			
ΔS_{sys}	ΔS_{surr}	ΔS_{univ}	Process Spontaneous?
+	+	+	Yes
—	—	—	No (reaction will occur in opposite direction)
+	—	?	Yes, if ΔS_{sys} has a larger magnitude than ΔS_{surr}
—	+	?	Yes, if ΔS_{surr} has a larger magnitude than ΔS_{sys}



The mineral stibnite contains Sb_2S_3 .

We can now understand why spontaneity is often dependent on temperature and thus why water spontaneously freezes below 0°C and melts above 0°C. The term ΔS_{surr} is temperature-dependent. Since

$$\Delta S_{\text{surr}} = -\frac{\Delta H}{T}$$

at constant pressure, the value of ΔS_{surr} changes markedly with temperature. The magnitude of ΔS_{surr} will be very small at high temperatures and will increase as the temperature decreases. That is, exothermicity is most important as a driving force at low temperatures.

16.4 Free Energy

The symbol G for free energy honors Josiah Willard Gibbs (1839–1903), who was professor of mathematical physics at Yale University from 1871 to 1903. He laid the foundations of many areas of thermodynamics, particularly as they apply to chemistry.

So far we have used ΔS_{univ} to predict the spontaneity of a process. However, another thermodynamic function is also related to spontaneity and is especially useful in dealing with the temperature dependence of spontaneity. This function is called the **free energy**, which is symbolized by G and defined by the relationship

$$G = H - TS$$

where H is the enthalpy, T is the Kelvin temperature, and S is the entropy.

For a process that occurs at constant temperature, the change in free energy (ΔG) is given by the equation

$$\Delta G = \Delta H - T\Delta S$$

Note that all quantities here refer to the system. From this point on we will follow the usual convention that when no subscript is included, the quantity refers to the system.

To see how this equation relates to spontaneity, we divide both sides of the equation by $-T$ to produce

$$-\frac{\Delta G}{T} = -\frac{\Delta H}{T} + \Delta S$$

Remember that at constant temperature and pressure

$$\Delta S_{\text{surr}} = -\frac{\Delta H}{T}$$

So we can write

$$-\frac{\Delta G}{T} = -\frac{\Delta H}{T} + \Delta S = \Delta S_{\text{surr}} + \Delta S = \Delta S_{\text{univ}}$$

We have shown that

$$\Delta S_{\text{univ}} = -\frac{\Delta G}{T} \quad \text{at constant } T \text{ and } P$$

This result is very important. It means that a process carried out at constant temperature and pressure will be spontaneous only if ΔG is negative. That is, *a process (at constant T and P) is spontaneous in the direction in which the free energy decreases* ($-\Delta G$ means $+\Delta S_{\text{univ}}$).

Now we have two functions that can be used to predict spontaneity: the entropy of the universe, which applies to all processes, and free energy, which can be used for processes carried out at constant temperature and pressure. Since so many chemical reactions occur under the latter conditions, free energy is the more useful to chemists.

Let's use the free energy equation to predict the spontaneity of the melting of ice:



for which $\Delta H^\circ = 6.03 \times 10^3 \text{ J/mol}$ and $\Delta S^\circ = 22.1 \text{ J/K} \cdot \text{mol}$

Results of the calculations of ΔS_{univ} and ΔG° at -10°C , 0°C , and 10°C are shown in Table 16.4. These data predict that the process is spontaneous at 10°C ; that is, ice melts at this temperature because ΔS_{univ} is positive and ΔG° is negative. The opposite is true at -10°C , where water freezes spontaneously.

Why is this so? The answer lies in the fact that ΔS_{sys} (ΔS°) and ΔS_{surr} oppose each other. The term ΔS° favors the melting of ice because of the increase in positional entropy, and ΔS_{surr} favors the freezing of water because it is an exothermic process. At temperatures below 0°C , the change of state occurs in the exothermic direction because ΔS_{surr} is larger in magnitude than ΔS_{sys} . But above 0°C the change occurs in the direction in which ΔS_{sys} is favorable, since in this case ΔS_{sys} is larger in magnitude than ΔS_{surr} . At 0°C the *opposing tendencies just balance*, and the two states coexist; there is no driving force in either direction. An equilibrium exists between the two states of water. Note that ΔS_{univ} is equal to 0 at 0°C .

We can reach the same conclusions by examining ΔG° . At -10°C , ΔG° is positive because the ΔH° term is larger than the $T\Delta S^\circ$ term. The opposite is true at 10°C . At 0°C , ΔH° is equal to $T\Delta S^\circ$ and ΔG° is equal to 0. This means that solid H_2O and liquid H_2O have the same free energy at 0°C ($\Delta G^\circ = G_{\text{liquid}} - G_{\text{solid}}$), and the system is at equilibrium.

We can understand the temperature dependence of spontaneity by examining the behavior of ΔG . For a process occurring at constant temperature and pressure,

$$\Delta G = \Delta H - T\Delta S$$

If ΔH and ΔS favor opposite processes, spontaneity will depend on temperature in such a way that the exothermic direction will be favored at low temperatures. For example, for the process



TABLE 16.4 Results of the Calculation of ΔS_{univ} and ΔG° for the Process $\text{H}_2\text{O}(s) \rightarrow \text{H}_2\text{O}(l)$ at -10°C , 0°C , and 10°C *

T ($^\circ\text{C}$)	T (K)	ΔH° (J/mol)	ΔS° (J/K · mol)	$\Delta S_{\text{surr}} = -\frac{\Delta H^\circ}{T}$ (J/K · mol)	$\Delta S_{\text{univ}} = \Delta S^\circ + \Delta S_{\text{surr}}$ (J/K · mol)	$T\Delta S^\circ$ (J/mol)	$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ (J/mol)
-10	263	6.03×10^3	22.1	-22.9	-0.8	5.81×10^3	$+2.2 \times 10^2$
0	273	6.03×10^3	22.1	-22.1	0	6.03×10^3	0
10	283	6.03×10^3	22.1	-21.3	+0.8	6.25×10^3	-2.2×10^2

*Note that at 10°C , ΔS° (ΔS_{sys}) controls, and the process occurs even though it is endothermic. At -10°C , the magnitude of ΔS_{surr} is larger than that of ΔS° , so the process is spontaneous in the opposite (exothermic) direction.

The superscript degree symbol ($^\circ$) indicates all substances are in their standard states.

To review the definitions of standard states, see page 260.

Note that although ΔH and ΔS are somewhat temperature dependent, it is a good approximation to assume they are constant over a relatively small temperature range.

TABLE 16.5 Various Possible Combinations of ΔH and ΔS for a Process and the Resulting Dependence of Spontaneity on Temperature

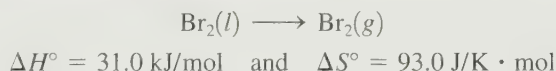
Case	Result
ΔS positive, ΔH negative	Spontaneous at all temperatures
ΔS positive, ΔH positive	Spontaneous at high temperatures (where exothermicity is relatively unimportant)
ΔS negative, ΔH negative	Spontaneous at low temperatures (where exothermicity is dominant)
ΔS negative, ΔH positive	Process not spontaneous at <i>any</i> temperature (reverse process is spontaneous at <i>all</i> temperatures)

ΔH is positive and ΔS is positive. The natural tendency for this system to lower its energy is in opposition to its natural tendency to increase its positional randomness. At low temperatures, ΔH dominates, and at high temperatures, ΔS dominates. The various possible cases are summarized in Table 16.5.

SAMPLE EXERCISE 16.5

Free Energy and Spontaneity

At what temperatures is the following process spontaneous at 1 atm?



What is the normal boiling point of liquid Br_2 ?

SOLUTION

The vaporization process will be spontaneous at all temperatures where ΔG° is negative. Note that ΔS° favors the vaporization process because of the increase in positional entropy, and ΔH° favors the *opposite* process, which is exothermic. These opposite tendencies will exactly balance at the boiling point of liquid Br_2 , since at this temperature liquid and gaseous Br_2 are in equilibrium ($\Delta G^\circ = 0$). We can find this temperature by setting $\Delta G^\circ = 0$ in the equation

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$0 = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta H^\circ = T\Delta S^\circ$$

Then

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{31.0 \times 10^4 \text{ J/mol}}{93.0 \text{ J/K} \cdot \text{mol}} = 333 \text{ K}$$

At temperatures above 333 K, $T\Delta S^\circ$ has a larger magnitude than ΔH° , and ΔG° (or $\Delta H^\circ - T\Delta S^\circ$) is negative. Above 333 K, the vaporization process is spontaneous; the opposite process occurs spontaneously below this temperature. At 333 K, liquid and gaseous Br_2 coexist in equilibrium. These observations can be summarized as follows (the pressure is 1 atm in each case):

1. $T > 333 \text{ K}$. The term ΔS° controls. The increase in entropy when liquid Br_2 is vaporized is dominant.
2. $T < 333 \text{ K}$. The process is spontaneous in the direction in which it is exothermic. The term ΔH° controls.

3. $T = 333\text{ K}$. The opposing driving forces are just balanced ($\Delta G^\circ = 0$), and the liquid and gaseous phases of bromine coexist. This is the normal boiling point.

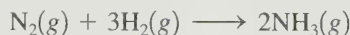
See Exercises 16.25 through 16.28.

16.5 Entropy Changes in Chemical Reactions

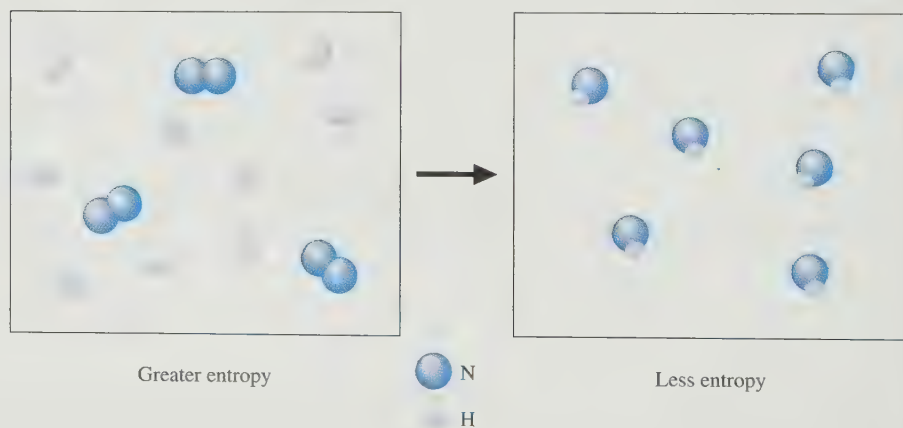
The second law of thermodynamics tells us that a process will be spontaneous if the entropy of the universe increases when the process occurs. We saw in Section 16.4 that for a process at constant temperature and pressure, we can use the change in free energy of the system to predict the sign of ΔS_{univ} and thus the direction in which it is spontaneous. So far we have applied these ideas only to physical processes, such as changes of state and the formation of solutions. However, the main business of chemistry is studying chemical reactions, and, therefore, we want to apply the second law to reactions.

First, we will consider the entropy changes accompanying chemical reactions that occur under conditions of constant temperature and pressure. As for the other types of processes we have considered, the entropy changes in the *surroundings* are determined by the heat flow that occurs as the reaction takes place. However, the entropy changes in the *system* (the reactants and products of the reaction) are determined by positional probability.

For example, in the ammonia synthesis reaction



four reactant molecules become two product molecules, lowering the number of independent units in the system, which leads to less positional disorder.

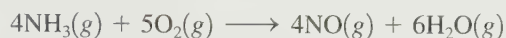


Fewer molecules mean fewer possible configurations. To help clarify this idea, consider a special container with a million compartments, each large enough to hold a hydrogen molecule. Thus there are a million ways one H_2 molecule can be placed in this container. But suppose we break the $\text{H}-\text{H}$ bond and place the two independent H atoms in the same container. A little thought will convince you that there are *many* more than a million ways to place the two separate atoms. The number of arrangements possible for the two independent atoms is much greater than the number for the molecule. Thus for the process



positional entropy increases.

Does positional entropy increase or decrease when the following reaction takes place?



In this case 9 gaseous molecules are changed to 10 gaseous molecules, and the positional entropy increases. There are more independent units as products than as reactants. In general, when a reaction involves gaseous molecules, *the change in positional entropy is dominated by the relative numbers of molecules of gaseous reactants and products*. If the number of molecules of the gaseous products is greater than the number of molecules of the gaseous reactants, positional entropy typically increases, and ΔS will be positive for the reaction.

SAMPLE EXERCISE 16.6

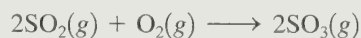
Predicting the Sign of ΔS°

Predict the sign of ΔS° for each of the following reactions.

- a. The thermal decomposition of solid calcium carbonate:



- b. The oxidation of SO_2 in air:



SOLUTION

- a. Since in this reaction a gas is produced from a solid reactant, the positional entropy increases, and ΔS° is positive.
- b. Here three molecules of gaseous reactants become two molecules of gaseous products. Since the number of gas molecules decreases, positional entropy decreases, and ΔS° is negative.

See Exercises 16.29 and 16.30.

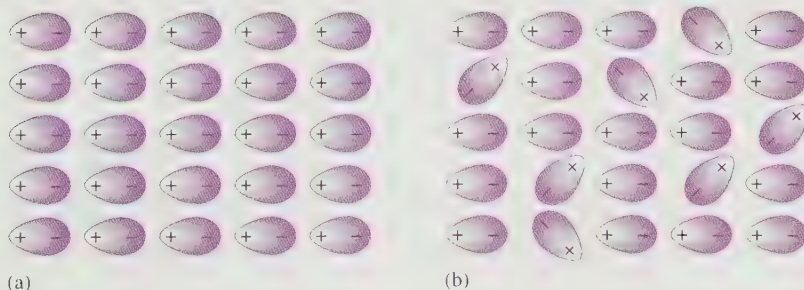
In thermodynamics it is the *change* in a certain function that is usually important. The change in enthalpy determines if a reaction is exothermic or endothermic at constant pressure. The change in free energy determines if a process is spontaneous at constant temperature and pressure. It is fortunate that changes in thermodynamic functions are sufficient for most purposes, since absolute values for many thermodynamic characteristics of a system, such as enthalpy or free energy, cannot be determined.

However, we can assign absolute entropy values. Consider a solid at 0 K, where molecular motion virtually ceases. If the substance is a perfect crystal, its internal arrangement is absolutely regular [see Fig. 16.5(a)]. There is only *one* way to achieve this perfect order: Every particle must be in its place. For example, with N coins

FIGURE 16.5

(a) A perfect crystal of hydrogen chloride at 0 K; the dipolar HCl molecules are represented by $\oplus \mid \ominus$. The entropy is zero ($S = 0$) for this perfect crystal at 0 K.

(b) As the temperature rises above 0 K, lattice vibrations allow some dipoles to change their orientations, producing some disorder and an increase in entropy ($S > 0$).



A perfect crystal at 0 K is an unattainable ideal, taken as a standard but never actually observed.

The standard entropy values represent the increase in entropy that occurs when a substance is heated from 0 K to 298 K at 1 atm pressure.

there is only one way to achieve the state of all heads. Thus a perfect crystal represents the lowest possible entropy; that is, *the entropy of a perfect crystal at 0 K is zero*. This is a statement of the **third law of thermodynamics**.

As the temperature of a perfect crystal is increased, the random vibrational motions increase, and disorder increases within the crystal [see Fig. 16.5(b)]. Thus the entropy of a substance increases with temperature. Since S is zero for a perfect crystal at 0 K, the entropy value for a substance at a particular temperature can be calculated by knowing the temperature dependence of entropy. (We will not show such calculations here.)

The *standard entropy values* S° of many common substances at 298 K and 1 atm are listed in Appendix 4. From these values you will see that the entropy of a substance does indeed increase in going from solid to liquid to gas. One especially interesting feature of this table is the very low S° value for diamond. The structure of diamond is highly ordered, with each carbon strongly bound to a tetrahedral arrangement of four other carbon atoms (see Section 10.5, Fig. 10.22). This type of structure allows very little disorder and has a very low entropy, even at 298 K. Graphite has a slightly higher entropy because its layered structure allows for a little more disorder.

Because *entropy is a state function of the system* (it is not pathway-dependent), the entropy change for a given chemical reaction can be calculated by taking the difference between the standard entropy values of products and those of the reactants:

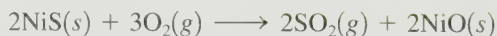
$$\Delta S^\circ_{\text{reaction}} = \sum n_p S^\circ_{\text{products}} - \sum n_r S^\circ_{\text{reactants}}$$

where, as usual, Σ represents the sum of the terms. It is important to note that entropy is an extensive property (it depends on the amount of substance present). This means that the number of moles of a given reactant (n_r) or product (n_p) must be taken into account.

SAMPLE EXERCISE 16.7

Calculating ΔS°

Calculate ΔS° at 25°C for the reaction



given the following standard entropy values:

Substance	S° (J/K · mol)
$\text{SO}_2(g)$	248
$\text{NiO}(s)$	38
$\text{O}_2(g)$	205
$\text{NiS}(s)$	53

SOLUTION

$$\begin{aligned}
 \text{Since } \Delta S^\circ &= \sum n_p S^\circ_{\text{products}} - \sum n_r S^\circ_{\text{reactants}} \\
 &= 2S^\circ_{\text{SO}_2(g)} + 2S^\circ_{\text{NiO}(s)} - 2S^\circ_{\text{NiS}(s)} - 3S^\circ_{\text{O}_2(g)} \\
 &= 2 \text{ mol} \left(248 \frac{\text{J}}{\text{K} \cdot \text{mol}} \right) + 2 \text{ mol} \left(38 \frac{\text{J}}{\text{K} \cdot \text{mol}} \right) \\
 &\quad - 2 \text{ mol} \left(53 \frac{\text{J}}{\text{K} \cdot \text{mol}} \right) - 3 \text{ mol} \left(205 \frac{\text{J}}{\text{K} \cdot \text{mol}} \right) \\
 &= 496 \text{ J/K} + 76 \text{ J/K} - 106 \text{ J/K} - 615 \text{ J/K} \\
 &= -149 \text{ J/K}
 \end{aligned}$$

We would expect ΔS° to be negative because the number of gaseous molecules decreases in this reaction.

See Exercise 16.33.

SAMPLE EXERCISE 16.8

Calculating ΔS°

Calculate ΔS° for the reduction of aluminum oxide by hydrogen gas:



Use the following standard entropy values:

Substance	S° (J/K · mol)
$\text{Al}_2\text{O}_3(s)$	51
$\text{H}_2(g)$	131
$\text{Al}(s)$	28
$\text{H}_2\text{O}(g)$	189

SOLUTION

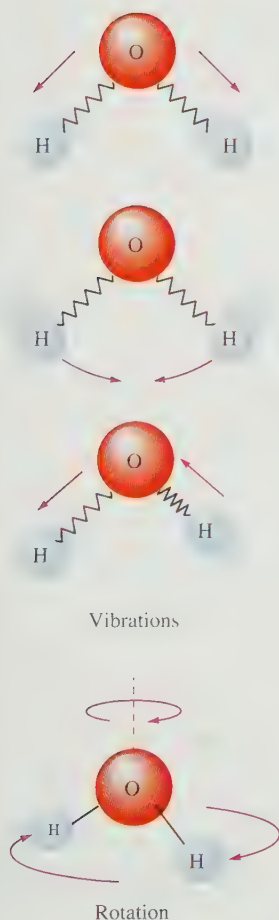
$$\begin{aligned}
 \Delta S^\circ &= \sum n_p S^\circ_{\text{products}} - \sum n_r S^\circ_{\text{reactants}} \\
 &= 2S^\circ_{\text{Al}(s)} + 3S^\circ_{\text{H}_2\text{O}(g)} - 3S^\circ_{\text{H}_2(g)} - S^\circ_{\text{Al}_2\text{O}_3(s)} \\
 &= 2 \text{ mol} \left(28 \frac{\text{J}}{\text{K} \cdot \text{mol}} \right) + 3 \text{ mol} \left(189 \frac{\text{J}}{\text{K} \cdot \text{mol}} \right) \\
 &\quad - 3 \text{ mol} \left(131 \frac{\text{J}}{\text{K} \cdot \text{mol}} \right) - 1 \text{ mol} \left(51 \frac{\text{J}}{\text{K} \cdot \text{mol}} \right) \\
 &= 56 \text{ J/K} + 567 \text{ J/K} - 393 \text{ J/K} - 51 \text{ J/K} \\
 &= 179 \text{ J/K}
 \end{aligned}$$

See Exercises 16.34 through 16.36.

The reaction considered in Sample Exercise 16.8 involves 3 moles of hydrogen gas on the reactant side and 3 moles of water vapor on the product side. Would you expect ΔS to be large or small for such a case? We have assumed that ΔS depends on the relative numbers of molecules of gaseous reactants and products. Based on this assumption, ΔS should be near zero for this reaction. However, ΔS is large and positive. Why is this so? The large value for ΔS results from the difference in the entropy values for hydrogen gas and water vapor. The reason for this difference can be traced to the difference in molecular structure. Because it is a nonlinear, triatomic molecule, H_2O has more rotational and vibrational motions (see Fig. 16.6) than does the diatomic H_2 molecule. Thus the standard entropy value for $\text{H}_2\text{O}(g)$ is greater than that for $\text{H}_2(g)$. Generally, *the more complex the molecule, the higher is the standard entropy value.*

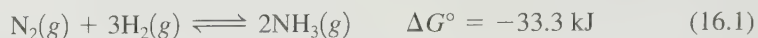
FIGURE 16.6

The H_2O molecule can vibrate and rotate in several ways, some of which are shown here. This freedom of motion leads to a higher entropy for water than for a substance like hydrogen, a simple diatomic molecule with fewer possible motions.



16.6 Free Energy and Chemical Reactions

For chemical reactions we are often interested in the **standard free energy change** (ΔG°), *the change in free energy that will occur if the reactants in their standard states are converted to the products in their standard states*. For example, for the ammonia synthesis reaction at 25°C,



This ΔG° value represents the change in free energy when 1 mol nitrogen gas at 1 atm reacts with 3 mol hydrogen gas at 1 atm to produce 2 mol gaseous NH_3 at 1 atm.

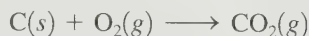
It is important to recognize that the standard free energy change for a reaction is not measured directly. For example, we can measure heat flow in a calorimeter to determine ΔH° , but we cannot measure ΔG° this way. The value of ΔG° for the ammonia synthesis in Equation (16.1) was *not* obtained by mixing 1 mol N_2 and 3 mol H_2 in a flask and measuring the change in free energy as 2 mol NH_3 formed. For one thing, if we mixed 1 mol N_2 and 3 mol H_2 in a flask, the system would go to equilibrium rather than to completion. Also, we have no instrument that measures free energy. However, while we cannot directly measure ΔG° for a reaction, we can calculate it from other measured quantities, as we will see later in this section.

Why is it useful to know ΔG° for a reaction? As we will see in more detail later in this chapter, knowing the ΔG° values for several reactions allows us to compare the relative tendency of these reactions to occur. The more negative the value of ΔG° , the further a reaction will go to the right to reach equilibrium. We must use standard-state free energies to make this comparison because free energy varies with pressure or concentration. Thus, to get an accurate comparison of reaction tendencies, we must compare all reactions under the same pressure or concentration conditions. We will have more to say about the significance of ΔG° later.

There are several ways to calculate ΔG° . One common method uses the equation

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

which applies to a reaction carried out at constant temperature. For example, for the reaction



the values of ΔH° and ΔS° are known to be -393.5 kJ and 3.05 J/K , respectively, and ΔG° can be calculated at 298 K as follows:

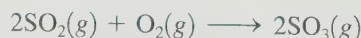
$$\begin{aligned} \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= -3.935 \times 10^5 \text{ J} - (298 \text{ K})(3.05 \text{ J/K}) \\ &= -3.944 \times 10^5 \text{ J} \\ &= -394.4 \text{ kJ (per mole of CO}_2\text{)} \end{aligned}$$

The value of ΔG° tells us nothing about the rate of a reaction, only its eventual equilibrium position.

SAMPLE EXERCISE 16.9

Calculating ΔH° , ΔS° , and ΔG°

Consider the reaction



carried out at 25°C and 1 atm. Calculate ΔH° , ΔS° , and ΔG° using the following data:

Substance	ΔH_f° (kJ/mol)	S° (J/K · mol)
$\text{SO}_2(g)$	-297	248
$\text{SO}_3(g)$	-396	257
$\text{O}_2(g)$	0	205

SOLUTION

The value of ΔH° can be calculated from the enthalpies of formation using the equation we discussed in Section 6.4:

$$\Delta H^\circ = \sum n_p \Delta H_f^\circ (\text{products}) - \sum n_r \Delta H_f^\circ (\text{reactants})$$

$$\begin{aligned}\text{Then } \Delta H^\circ &= 2\Delta H_f^\circ (\text{SO}_3(g)) - 2\Delta H_f^\circ (\text{SO}_2(g)) - \Delta H_f^\circ (\text{O}_2(g)) \\ &= 2 \text{ mol}(-396 \text{ kJ/mol}) - 2 \text{ mol}(-297 \text{ kJ/mol}) - 0 \\ &= -792 \text{ kJ} + 594 \text{ kJ} \\ &= -198 \text{ kJ}\end{aligned}$$

The value of ΔS° can be calculated using the standard entropy values and the equation discussed in Section 16.5:

$$\Delta S^\circ = \sum n_p S_{\text{products}}^\circ - \sum n_r S_{\text{reactants}}^\circ$$

Thus

$$\begin{aligned}\Delta S^\circ &= 2S_{\text{SO}_3(g)}^\circ - 2S_{\text{SO}_2(g)}^\circ - S_{\text{O}_2(g)}^\circ \\ &= 2 \text{ mol}(257 \text{ J/K} \cdot \text{mol}) - 2 \text{ mol}(248 \text{ J/K} \cdot \text{mol}) - 1 \text{ mol}(205 \text{ J/K} \cdot \text{mol}) \\ &= 514 \text{ J/K} - 496 \text{ J/K} - 205 \text{ J/K} \\ &= -187 \text{ J/K}\end{aligned}$$

We would expect ΔS° to be negative because three molecules of gaseous reactants give two molecules of gaseous products.

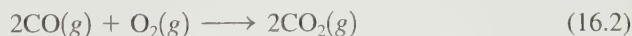
The value of ΔG° can now be calculated from the equation

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= -198 \text{ kJ} - (298 \text{ K})\left(-187 \frac{\text{J}}{\text{K}}\right)\left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right) \\ &= -198 \text{ kJ} + 55.7 \text{ kJ} = -142 \text{ kJ}\end{aligned}$$

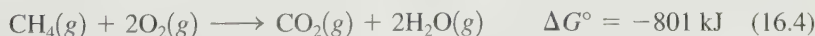
See Exercises 16.41 and 16.42.

A second method for calculating ΔG for a reaction takes advantage of the fact that, like enthalpy, *free energy is a state function*. Therefore, we can use procedures for finding ΔG that are similar to those for finding ΔH using Hess's law.

To illustrate this method for calculating the free energy change, we will obtain ΔG° for the reaction



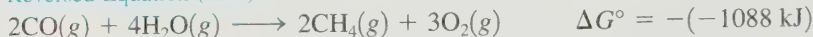
from the following data:



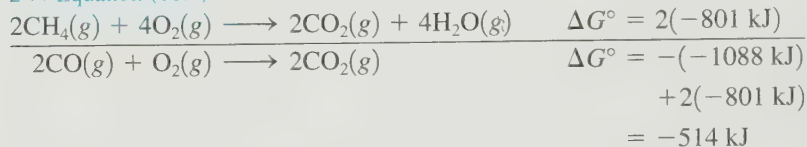
Note that $\text{CO}(g)$ is a reactant in Equation (16.2). This means that Equation (16.3) must be reversed, since $\text{CO}(g)$ is a product in that reaction as written. When a

reaction is reversed, the sign of ΔG° is also reversed. In Equation (16.4), $\text{CO}_2(g)$ is a product, as it is in Equation (16.2), but only one molecule of CO_2 is formed. Thus Equation (16.4) must be multiplied by 2, which means the ΔG° value for Equation (16.4) also must be multiplied by 2. Free energy is an extensive property, since it is defined by two extensive properties, H and S .

Reversed Equation (16.3)

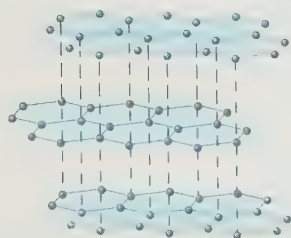


$2 \times$ Equation (16.4)

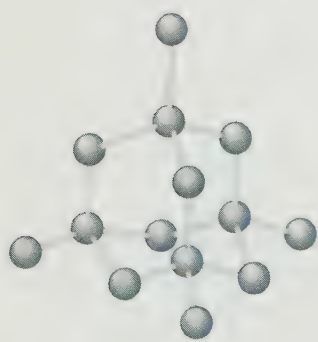


This example shows that the ΔG values for reactions are manipulated in exactly the same way as the ΔH values.

SAMPLE EXERCISE 16.10



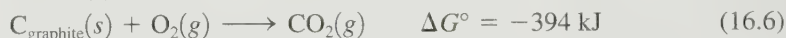
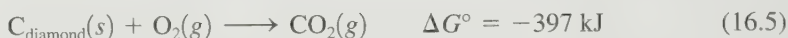
Graphite



Diamond

Calculating ΔG°

Using the following data (at 25°C)



calculate ΔG° for the reaction

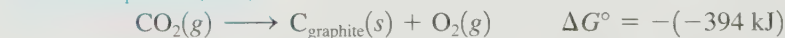


SOLUTION

We reverse Equation (16.6) to make graphite a product, as required, and then add the new equation to Equation (16.5):



Reversed Equation (16.6)



Since ΔG° is negative for this process, diamond should spontaneously change to graphite at 25°C and 1 atm. However, the reaction is so slow under these conditions that we do not observe the process. This is another example of kinetic rather than thermodynamic control of a reaction. We can say that diamond is kinetically stable with respect to graphite even though it is thermodynamically unstable.

See Exercises 16.45 and 16.46.

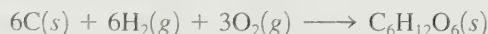
In Sample Exercise 16.10 we saw that the process



is spontaneous but very slow at 25°C and 1 atm. The reverse process can be made to occur at high temperatures and pressures. Diamond has a more compact structure and thus a higher density than graphite, so exerting very high pressure causes it to

become thermodynamically favored. If high temperatures are also used to make the process fast enough to be feasible, diamonds can be made from graphite. The conditions typically used involve temperatures greater than 1000°C and pressures of about 10^5 atm. About half of all industrial diamonds are made this way.

A third method for calculating the free energy change for a reaction uses standard free energies of formation. The **standard free energy of formation** (ΔG_f°) of a substance is defined as the *change in free energy that accompanies the formation of 1 mole of that substance from its constituent elements with all reactants and products in their standard states*. For the formation of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$), the appropriate reaction is



The standard free energy associated with this process is called the *free energy of formation of glucose*. Values of the standard free energy of formation are useful in calculating ΔG° for specific chemical reactions using the equation

$$\Delta G^\circ = \sum n_p \Delta G_f^\circ (\text{products}) - \sum n_r \Delta G_f^\circ (\text{reactants})$$

Values of ΔG_f° for many common substances are listed in Appendix 4. Note that, analogous to the enthalpy of formation, *the standard free energy of formation of an element in its standard state is zero*. Also note that the number of moles of each reactant (n_r) and product (n_p) must be used when calculating ΔG° for a reaction.

The standard state of an element is its most stable state of 25°C and 1 atm.

Calculating ΔG° is very similar to calculating ΔH° , as shown in Section 6.4.

SAMPLE EXERCISE 16.11

Calculating ΔG°

Methanol is a high-octane fuel used in high-performance racing engines. Calculate ΔG° for the reaction



given the following free energies of formation:

Substance	ΔG_f° (kJ/mol)
$\text{CH}_3\text{OH}(g)$	-163
$\text{O}_2(g)$	0
$\text{CO}_2(g)$	-394
$\text{H}_2\text{O}(g)$	-229

SOLUTION

We use the equation

$$\begin{aligned} \Delta G^\circ &= \sum n_p \Delta G_f^\circ (\text{products}) - \sum n_r \Delta G_f^\circ (\text{reactants}) \\ &= 2\Delta G_f^\circ (\text{CO}_2(g)) + 4\Delta G_f^\circ (\text{H}_2\text{O}(g)) - 3\Delta G_f^\circ (\text{O}_2(g)) - 2\Delta G_f^\circ (\text{CH}_3\text{OH}(g)) \\ &= 2 \text{ mol}(-394 \text{ kJ/mol}) + 4 \text{ mol}(-229 \text{ kJ/mol}) - 3(0) \\ &\quad - 2 \text{ mol}(-163 \text{ kJ/mol}) \\ &= -1378 \text{ kJ} \end{aligned}$$

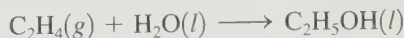
The large magnitude and the negative sign of ΔG° indicate that this reaction is very favorable thermodynamically.

See Exercises 16.47 through 16.49.

SAMPLE EXERCISE 16.12

Free Energy and Spontaneity

A chemical engineer wants to determine the feasibility of making ethanol ($\text{C}_2\text{H}_5\text{OH}$) by reacting water with ethylene (C_2H_4) according to the equation



Is this reaction spontaneous under standard conditions?

SOLUTION

To determine the spontaneity of this reaction under standard conditions, we must determine ΔG° for the reaction. We can do this using standard free energies of formation at 25°C from Appendix 4:

$$\Delta G_f^\circ(\text{C}_2\text{H}_5\text{OH}(l)) = -175 \text{ kJ/mol}$$

$$\Delta G_f^\circ(\text{H}_2\text{O}(l)) = -237 \text{ kJ/mol}$$

$$\Delta G_f^\circ(\text{C}_2\text{H}_4(g)) = 68 \text{ kJ/mol}$$

$$\begin{aligned}\text{Then } \Delta G^\circ &= \Delta G_f^\circ(\text{C}_2\text{H}_5\text{OH}(l)) - \Delta G_f^\circ(\text{H}_2\text{O}(l)) - \Delta G_f^\circ(\text{C}_2\text{H}_4(g)) \\ &= -175 \text{ kJ} - (-237 \text{ kJ}) - 68 \text{ kJ} \\ &= -6 \text{ kJ}\end{aligned}$$

Thus the process is spontaneous under standard conditions at 25°C .

See Exercise 16.50.

Although the reaction considered in Sample Exercise 16.12 is spontaneous, other features of the reaction must be studied to see if the process is feasible. For example, the chemical engineer will need to study the kinetics of the reaction to determine whether it is fast enough to be useful and, if it is not, whether a catalyst can be found to enhance the rate. In doing these studies, the engineer must remember that ΔG° depends on temperature:

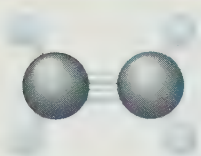
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Thus, if the process must be carried out at high temperatures to be fast enough to be feasible, ΔG° must be recalculated at that temperature from the ΔH° and ΔS° values for the reaction.

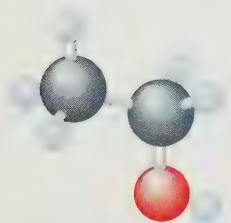
16.7 The Dependence of Free Energy on Pressure

In this chapter we have seen that a system at constant temperature and pressure will proceed spontaneously in the direction that lowers its free energy. This is why reactions proceed until they reach equilibrium. As we will see later in this section, *the equilibrium position represents the lowest free energy value available to a particular reaction system*. The free energy of a reaction system changes as the reaction proceeds, because free energy is dependent on the pressure of a gas or on the concentration of species in solution. We will deal only with the pressure dependence of the free energy of an ideal gas. The dependence of free energy on concentration can be developed using similar reasoning.

To understand the pressure dependence of free energy, we need to know how pressure affects the thermodynamic functions that comprise free energy, that is,



Ethylene.



Ethanol.

enthalpy and entropy (recall that $G = H - TS$). For an ideal gas, enthalpy is not pressure-dependent. However, entropy *does* depend on pressure because of its dependence on volume. Consider 1 mole of an ideal gas at a given temperature. At a volume of 10.0 L, the gas has many more positions available for its molecules than if its volume is 1.0 L. The positional entropy is greater in the larger volume. In summary, at a given temperature for 1 mole of ideal gas

$$S_{\text{large volume}} > S_{\text{small volume}}$$

or, since pressure and volume are inversely related,

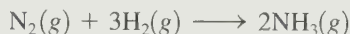
$$S_{\text{low pressure}} > S_{\text{high pressure}}$$

We have shown qualitatively that the entropy and therefore the free energy of an ideal gas depend on its pressure. Using a more detailed argument, which we will not consider here, it can be shown that

$$G = G^\circ + RT \ln(P)$$

where G° is the free energy of the gas at a pressure of 1 atm, G is the free energy of the gas at a pressure of P atm, R is the universal gas constant, and T is the Kelvin temperature.

To see how the change in free energy for a reaction depends on pressure, we will consider the ammonia synthesis reaction



In general,

$$\Delta G = \sum n_{\text{p}} G_{\text{products}} - \sum n_{\text{r}} G_{\text{reactants}}$$

For this reaction

$$\Delta G = 2G_{\text{NH}_3} - G_{\text{N}_2} - 3G_{\text{H}_2}$$

where

$$G_{\text{NH}_3} = G_{\text{NH}_3}^\circ + RT \ln(P_{\text{NH}_3})$$

$$G_{\text{N}_2} = G_{\text{N}_2}^\circ + RT \ln(P_{\text{N}_2})$$

$$G_{\text{H}_2} = G_{\text{H}_2}^\circ + RT \ln(P_{\text{H}_2})$$

Substituting these values into the equation gives

$$\begin{aligned} \Delta G &= 2[G_{\text{NH}_3}^\circ + RT \ln(P_{\text{NH}_3})] - [G_{\text{N}_2}^\circ + RT \ln(P_{\text{N}_2})] - 3[G_{\text{H}_2}^\circ + RT \ln(P_{\text{H}_2})] \\ &= 2G_{\text{NH}_3}^\circ - G_{\text{N}_2}^\circ - 3G_{\text{H}_2}^\circ + 2RT \ln(P_{\text{NH}_3}) - RT \ln(P_{\text{N}_2}) - 3RT \ln(P_{\text{H}_2}) \\ &= \underbrace{(2G_{\text{NH}_3}^\circ - G_{\text{N}_2}^\circ - 3G_{\text{H}_2}^\circ)}_{\Delta G^\circ_{\text{reaction}}} + RT[2 \ln(P_{\text{NH}_3}) - \ln(P_{\text{N}_2}) - 3 \ln(P_{\text{H}_2})] \end{aligned}$$

The first term (in parentheses) is ΔG° for the reaction. Thus we have

$$\Delta G = \Delta G^\circ_{\text{reaction}} + RT[2 \ln(P_{\text{NH}_3}) - \ln(P_{\text{N}_2}) - 3 \ln(P_{\text{H}_2})]$$

and since

$$2 \ln(P_{\text{NH}_3}) = \ln(P_{\text{NH}_3}^2)$$

$$-\ln(P_{\text{N}_2}) = \ln\left(\frac{1}{P_{\text{N}_2}}\right)$$

$$-3 \ln(P_{\text{H}_2}) = \ln\left(\frac{1}{P_{\text{H}_2}^3}\right)$$

the equation becomes

$$\Delta G = \Delta G^\circ + RT \ln\left(\frac{P_{\text{NH}_3}^2}{(P_{\text{N}_2})(P_{\text{H}_2}^3)}\right)$$

See Appendix 1.2 to review logarithms.

$$\text{But the term } \frac{P_{\text{NH}_3}^2}{(P_{\text{N}_2})(P_{\text{H}_2}^3)}$$

is the reaction quotient Q discussed in Section 13.5. Therefore, we have

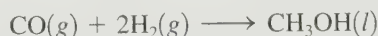
$$\Delta G = \Delta G^\circ + RT \ln(Q)$$

where Q is the reaction quotient (from the law of mass action), T is the temperature (K), R is the gas law constant and is equal to $8.3145 \text{ J/K} \cdot \text{mol}$, ΔG° is the free energy change for the reaction with all reactants and products at a pressure of 1 atm, and ΔG is the free energy change for the reaction for the specified pressures of reactants and products.

SAMPLE EXERCISE 16.13

Calculating ΔG°

One method for synthesizing methanol (CH_3OH) involves reacting carbon monoxide and hydrogen gases:



Calculate ΔG at 25°C for this reaction where carbon monoxide gas at 5.0 atm and hydrogen gas at 3.0 atm are converted to liquid methanol.

SOLUTION

To calculate ΔG for this process, we use the equation

$$\Delta G = \Delta G^\circ + RT \ln(Q)$$

We must first compute ΔG° from standard free energies of formation (see Appendix 4). Since

$$\Delta G_{\text{f}}^\circ (\text{CH}_3\text{OH}(l)) = -166 \text{ kJ}$$

$$\Delta G_{\text{f}}^\circ (\text{H}_2(g)) = 0$$

$$\Delta G_{\text{f}}^\circ (\text{CO}(g)) = -137 \text{ kJ}$$

$$\Delta G^\circ = -166 \text{ kJ} - (-137 \text{ kJ}) - 0 = -29 \text{ kJ} = -2.9 \times 10^4 \text{ J}$$

Note that this is the value of ΔG° for the reaction of 1 mol CO with 2 mol H_2 to produce 1 mol CH_3OH . We might call this the value of ΔG° for one “round” of the reaction or for one mole of the reaction. Thus the ΔG° value might better be written as $-2.9 \times 10^4 \text{ J/mol of reaction}$, or $-2.9 \times 10^4 \text{ J/mol rxn}$.

We can now calculate ΔG using

$$\Delta G^\circ = -2.9 \times 10^4 \text{ J/mol rxn}$$

$$R = 8.3145 \text{ J/K} \cdot \text{mol}$$

$$T = 273 + 25 = 298 \text{ K}$$

$$Q = \frac{1}{(P_{\text{CO}})(P_{\text{H}_2}^2)} = \frac{1}{(5.0)(3.0)^2} = 2.2 \times 10^{-2}$$

Note that the pure liquid methanol is not included in the calculation of Q . Then

$$\begin{aligned} \Delta G &= \Delta G^\circ + RT \ln(Q) \\ &= (-2.9 \times 10^4 \text{ J/mol rxn}) + (8.3145 \text{ J/K} \cdot \text{mol rxn})(298 \text{ K}) \ln(2.2 \times 10^{-2}) \\ &= (-2.9 \times 10^4 \text{ J/mol rxn}) - (9.4 \times 10^3 \text{ J/mol rxn}) = -3.8 \times 10^4 \text{ J/mol rxn} \\ &= -38 \text{ kJ/mol rxn} \end{aligned}$$

Note in this case that ΔG is defined for “one mole of the reaction,” that is, for 1 mol $\text{CO}(g)$ reacting with 2 mol $\text{H}_2(g)$ to form 1 mol $\text{CH}_3\text{OH}(l)$. Thus ΔG , ΔG° , and $RT \ln(Q)$ all have units of J/mol of reaction. In this case the units of R are actually $\text{J/K} \cdot \text{mol of reaction}$, although they are usually not written this way.

Note that ΔG is significantly more negative than ΔG° , implying that the reaction is more spontaneous at reactant pressures greater than 1 atm. We might expect this result from Le Châtelier's principle.

See Exercises 16.51 and 16.52.

The Meaning of ΔG for a Chemical Reaction

In this section we have learned to calculate ΔG for chemical reactions under various conditions. For example, in Sample Exercise 16.13 the calculations show that the formation of $\text{CH}_3\text{OH}(l)$ from $\text{CO}(g)$ at 5.0 atm reacting with $\text{H}_2(g)$ at 3.0 atm is spontaneous. What does this result mean? Does it mean that if we mixed 1.0 mol $\text{CO}(g)$ and 2.0 mol $\text{H}_2(g)$ together at pressures of 5.0 and 3.0 atm, respectively, that 1.0 mol $\text{CH}_3\text{OH}(l)$ would form in the reaction flask? The answer is no. This answer may surprise you in view of what has been said in this section. It is true that 1.0 mol $\text{CH}_3\text{OH}(l)$ has a lower free energy than 1.0 mol $\text{CO}(g)$ at 5.0 atm plus 2.0 mol $\text{H}_2(g)$ at 3.0 atm. However, when $\text{CO}(g)$ and $\text{H}_2(g)$ are mixed under these conditions, there is *an even lower free energy available to this system than 1.0 mol pure $\text{CH}_3\text{OH}(l)$* . For reasons we will discuss shortly, *the system can achieve the lowest possible free energy by going to equilibrium, not by going to completion*. At the equilibrium position, some of the $\text{CO}(g)$ and $\text{H}_2(g)$ will remain in the reaction flask. So even though 1.0 mol pure $\text{CH}_3\text{OH}(l)$ is at a lower free energy than 1.0 mol $\text{CO}(g)$ and 2.0 mol $\text{H}_2(g)$ at 5.0 and 3.0 atm, respectively, the reaction system will stop short of forming 1.0 mol $\text{CH}_3\text{OH}(l)$. The reaction stops short of completion because the equilibrium mixture of $\text{CH}_3\text{OH}(l)$, $\text{CO}(g)$, and $\text{H}_2(g)$ exists at the lowest possible free energy available to the system.

To illustrate this point, we will explore a mechanical example. Consider balls rolling down the two hills shown in Fig. 16.7. Note that in both cases point B has a lower potential energy than point A.

In Fig. 16.7(a) the ball will roll to point B. This diagram is analogous to a phase change. For example, at 25°C ice will spontaneously change completely to liquid water, because the latter has the lowest free energy. In this case liquid water is the only choice. There is no intermediate mixture of ice and water with lower free energy.

The situation is different for a chemical reaction system, as illustrated in Fig. 16.7(b). In Fig. 16.7(b) the ball will not get to point B because there is a lower potential energy at point C. Like the ball, a chemical system will seek the *lowest possible free energy*, which, for reasons we will discuss below, is the equilibrium position.

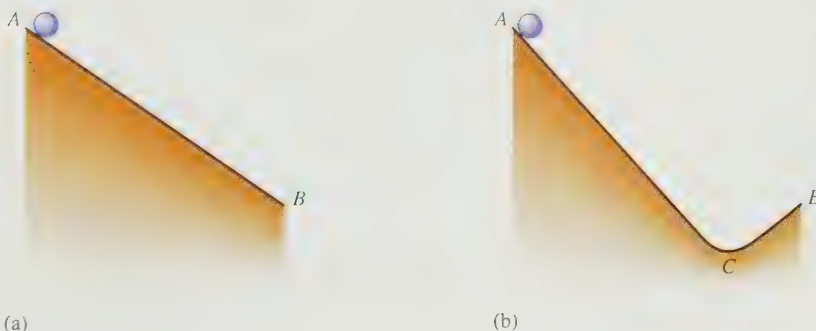


FIGURE 16.7
Schematic representations of balls rolling down two types of hills.

Therefore, although the value of ΔG for a given reaction system tells us whether the products or reactants are favored under a given set of conditions, it does not mean that the system will proceed to pure products (if ΔG is negative) or remain at pure reactants (if ΔG is positive). Instead, the system will spontaneously go to the equilibrium position, the lowest possible free energy available to it. In the next section we will see that the value of ΔG° for a particular reaction tells us exactly where this position will be.

16.8 Free Energy and Equilibrium

When the components of a given chemical reaction are mixed, they will proceed, rapidly or slowly depending on the kinetics of the process, to the equilibrium position. In Chapter 13 we defined the equilibrium position as the point at which the forward and reverse reaction rates are equal. In this chapter we look at equilibrium from a thermodynamic point of view, and we find that the **equilibrium point occurs at the lowest value of free energy available to the reaction system**. As it turns out, the two definitions give the same equilibrium state, which must be the case for both the kinetic and thermodynamic models to be valid.

To understand the relationship of free energy to equilibrium, let's consider the following simple hypothetical reaction:



where 1.0 mole of gaseous A is initially placed in a reaction vessel at a pressure of 2.0 atm. The free energies for A and B are diagrammed as shown in Fig. 16.8(a). As A reacts to form B, the total free energy of the system changes, yielding the following results:

$$\text{Free energy of A} = G_A = G_A^\circ + RT \ln(P_A)$$

$$\text{Free energy of B} = G_B = G_B^\circ + RT \ln(P_B)$$

$$\text{Total free energy of system} = G = G_A + G_B$$

As A changes to B, G_A will decrease because P_A is decreasing [Fig. 16.8(b)]. In contrast, G_B will increase because P_B is increasing. The reaction will proceed to the right as long as the total free energy of the system decreases (as long as G_B is less than G_A). At some point the pressures of A and B reach the values P_A^e and P_B^e that make G_A equal to G_B . *The system has reached equilibrium* [Fig. 16.8(c)]. Since A at pressure P_A^e and B at pressure P_B^e have the same free energy (G_A equals G_B), ΔG is zero for A at pressure P_A^e changing to B at pressure P_B^e . *The system has reached minimum free energy*. There is no longer any driving force to change A to B or B to A, so the system remains at this position (the pressures of A and B remain constant).

Suppose that for the experiment described above the plot of free energy versus the mole fraction of A reacted is defined as shown in Fig. 16.9(a). In this experiment, minimum free energy is reached when 75% of A has been changed to B. At this point, the pressure of A is 0.25 times the original pressure, or

$$(0.25)(2.0 \text{ atm}) = 0.50 \text{ atm}$$

The pressure of B is

$$(0.75)(2.0 \text{ atm}) = 1.5 \text{ atm}$$

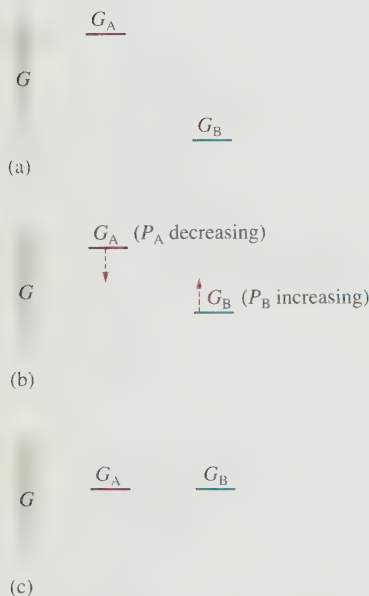
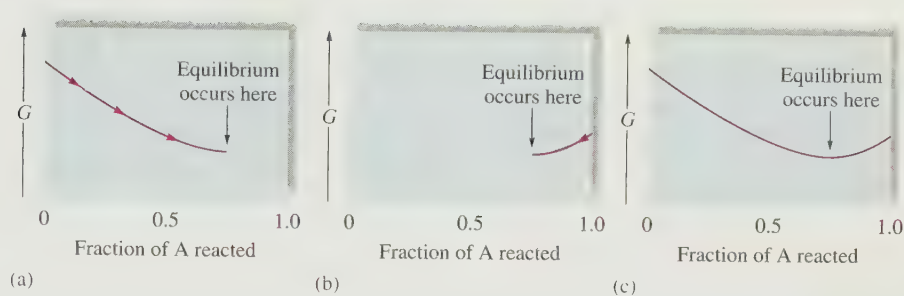


FIGURE 16.8

(a) The initial free energies of A and B. (b) As A(g) changes to B(g) , the free energy of A decreases and that of B increases. (c) Eventually, pressures of A and B are achieved such that $G_A = G_B$, the equilibrium position.

FIGURE 16.9

(a) The change in free energy to reach equilibrium, beginning with 1.0 mol A(g) at $P_A = 2.0$ atm. (b) The change in free energy to reach equilibrium, beginning with 1.0 mol B(g) at $P_B = 2.0$ atm. (c) The free energy profile for $A(g) \rightleftharpoons B(g)$ in a system containing 1.0 mol (A plus B) at $P_{\text{TOTAL}} = 2.0$ atm. Each point on the curve corresponds to the total free energy of the system for a given combination of A and B.



Since this is the equilibrium position, we can use the equilibrium pressures to calculate a value for K for the reaction in which A is converted to B at this temperature:

$$K = \frac{P_B^e}{P_A^e} = \frac{1.5 \text{ atm}}{0.50 \text{ atm}} = 3.0$$

Exactly the same equilibrium point would be achieved if we placed 1.0 mol pure B(g) in the flask at a pressure of 2.0 atm. In this case B would change to A until equilibrium ($G_B = G_A$) is reached. This is shown in Fig. 16.9(b).

The overall free energy curve for this system is shown in Fig. 16.9(c). Note that any mixture of A(g) and B(g) containing 1.0 mol (A plus B) at a total pressure of 2.0 atm will react until it reaches the minimum in the curve.

In summary, when substances undergo a chemical reaction, the reaction proceeds to the minimum free energy (equilibrium), which corresponds to the point where

$$G_{\text{products}} = G_{\text{reactants}} \quad \text{or} \quad \Delta G = G_{\text{products}} - G_{\text{reactants}} = 0$$

We can now establish a quantitative relationship between free energy and the value of the equilibrium constant. We have seen that

$$\Delta G = \Delta G^\circ + RT \ln(Q)$$

and at equilibrium ΔG equals 0 and Q equals K .

$$\text{So} \quad \Delta G = 0 = \Delta G^\circ + RT \ln(K)$$

$$\text{or} \quad \Delta G^\circ = -RT \ln(K)$$

We must note the following characteristics of this very important equation.

Case 1: $\Delta G^\circ = 0$. When ΔG° equals zero for a particular reaction, the free energies of the reactants and products are equal when all components are in the standard states (1 atm for gases). The system is at equilibrium when the pressures of all reactants and products are 1 atm, which means that K equals 1.

Case 2: $\Delta G^\circ < 0$. In this case ΔG° ($G_{\text{products}}^\circ - G_{\text{reactants}}^\circ$) is negative, which means that

$$G_{\text{products}}^\circ < G_{\text{reactants}}^\circ$$

If a flask contains the reactants and products, all at 1 atm, the system will *not* be at equilibrium. Since $G_{\text{products}}^\circ$ is less than $G_{\text{reactants}}^\circ$, the system will adjust to the right to reach equilibrium. In this case K will be *greater than 1*, since the pressures of the products at equilibrium will be greater than 1 atm and the pressures of the reactants at equilibrium will be less than 1 atm.

For the reaction $A(g) \rightleftharpoons B(g)$, the pressure is constant during the reaction, since the same number of gas molecules is always present.

TABLE 16.6

Qualitative Relationship Between the Change in Standard Free Energy and the Equilibrium Constant for a Given Reaction

ΔG°	K
$\Delta G^\circ = 0$	$K = 1$
$\Delta G^\circ < 0$	$K > 1$
$\Delta G^\circ > 0$	$K < 1$

Case 3: $\Delta G^\circ > 0$. Since $\Delta G^\circ (G^\circ_{\text{products}} - G^\circ_{\text{reactants}})$ is positive,

$$G^\circ_{\text{reactants}} < G^\circ_{\text{products}}$$

If a flask contains the reactants and products, all at 1 atm, the system will *not* be at equilibrium. In this case the system will adjust to the left (toward the reactants, which have a lower free energy) to reach equilibrium. The value of K will be *less than 1*, since at equilibrium the pressures of the reactants will be greater than 1 atm and the pressures of the products will be less than 1 atm.

These results are summarized in Table 16.6. The value of K for a specific reaction can be calculated from the equation

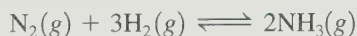
$$\Delta G^\circ = -RT \ln(K)$$

as is shown in Sample Exercises 16.14 and 16.15.

SAMPLE EXERCISE 16.14

Free Energy and Equilibrium I

Consider the ammonia synthesis reaction



where $\Delta G^\circ = -33.3$ kJ per mole of N_2 consumed at 25°C . For each of the following mixtures of reactants and products at 25°C , predict the direction in which the system will shift to reach equilibrium.

- $P_{\text{NH}_3} = 1.00$ atm, $P_{\text{N}_2} = 1.47$ atm, $P_{\text{H}_2} = 1.00 \times 10^{-2}$ atm
- $P_{\text{NH}_3} = 1.00$ atm, $P_{\text{N}_2} = 1.00$ atm, $P_{\text{H}_2} = 1.00$ atm

SOLUTION

- We can predict the direction of reaction to equilibrium by calculating the value of ΔG using the equation

$$\Delta G = \Delta G^\circ + RT \ln(Q)$$

$$\text{where } Q = \frac{P_{\text{NH}_3}^2}{(P_{\text{N}_2})(P_{\text{H}_2})^3} = \frac{(1.00)^2}{(1.47)(1.00 \times 10^{-2})^3} = 6.80 \times 10^5$$

$$T = 25 + 273 = 298 \text{ K}$$

$$R = 8.3145 \text{ J/K} \cdot \text{mol}$$

and

$$\Delta G^\circ = -33.3 \text{ kJ/mol} = -3.33 \times 10^4 \text{ J/mol}$$

Then

$$\begin{aligned} \Delta G &= (-3.33 \times 10^4 \text{ J/mol}) + (8.3145 \text{ J/K} \cdot \text{mol})(298 \text{ K}) \ln(6.8 \times 10^5) \\ &= (-3.33 \times 10^4 \text{ J/mol}) + (3.33 \times 10^4 \text{ J/mol}) = 0 \end{aligned}$$

Since $\Delta G = 0$, the reactants and products have the same free energies at these partial pressures. The system is already at equilibrium, and no shift will occur.

- The partial pressures given here are all 1.00 atm, which means that the system is in the standard state. That is,

The units of ΔG , ΔG° , and $RT \ln(Q)$ all refer to the balanced reaction with all amounts expressed in moles. We might say that the units are joules per "mole of reaction," although only the "per mole" is indicated for R (as is customary).

$$\begin{aligned}\Delta G &= \Delta G^\circ + RT \ln(Q) = \Delta G^\circ + RT \ln \frac{(1.00)^2}{(1.00)(1.00)^3} \\ &= \Delta G^\circ + RT \ln(1.00) = \Delta G^\circ + 0 = \Delta G^\circ\end{aligned}$$

For this reaction at 25°C,

$$\Delta G^\circ = -33.3 \text{ kJ/mol}$$

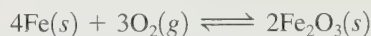
The negative value for ΔG° means that in their standard states the products have a lower free energy than the reactants. Thus the system will move to the right to reach equilibrium. That is, K is greater than 1.

See Exercise 16.53.

SAMPLE EXERCISE 16.15

Free Energy and Equilibrium II

The overall reaction for the corrosion (rusting) of iron by oxygen is



Using the following data, calculate the equilibrium constant for this reaction at 25°C.

Substance	ΔH_f° (kJ/mol)	S° (J/K · mol)
$\text{Fe}_2\text{O}_3(s)$	-826	90
$\text{Fe}(s)$	0	27
$\text{O}_2(g)$	0	205

SOLUTION

To calculate K for this reaction, we will use the equation

$$\Delta G^\circ = -RT \ln(K)$$

We must first calculate ΔG° from

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

where

$$\begin{aligned}\Delta H^\circ &= 2\Delta H_f^\circ(\text{Fe}_2\text{O}_3(s)) - 3\Delta H_f^\circ(\text{O}_2(g)) - 4\Delta H_f^\circ(\text{Fe}(s)) \\ &= 2 \text{ mol}(-826 \text{ kJ/mol}) - 0 - 0 \\ &= -1652 \text{ kJ} = -1.652 \times 10^6 \text{ J}\end{aligned}$$

$$\begin{aligned}\Delta S^\circ &= 2S_{\text{Fe}_2\text{O}_3}^\circ - 3S_{\text{O}_2}^\circ - 4S_{\text{Fe}}^\circ \\ &= 2 \text{ mol}(90 \text{ J/K} \cdot \text{mol}) - 3 \text{ mol}(205 \text{ J/K} \cdot \text{mol}) - 4 \text{ mol}(27 \text{ J/K} \cdot \text{mol}) \\ &= -543 \text{ J/K}\end{aligned}$$

and

$$T = 273 + 25 = 298 \text{ K}$$

$$\begin{aligned}\text{Then } \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ = (-1.652 \times 10^6 \text{ J}) - (298 \text{ K})(-543 \text{ J/K}) \\ &= -1.490 \times 10^6 \text{ J}\end{aligned}$$

and

$$\Delta G^\circ = -RT \ln(K) = -1.490 \times 10^6 \text{ J} = -(8.3145 \text{ J/K} \cdot \text{mol})(298 \text{ K}) \ln(K)$$



Formation of rust on bare steel is a spontaneous process.

$$\text{Thus} \quad \ln(K) = \frac{1.490 \times 10^6}{2.48 \times 10^3} = 601$$

$$\text{and} \quad K = e^{601}$$

This is a very large equilibrium constant. The rusting of iron is clearly very favorable from a thermodynamic point of view.

See Exercise 16.56.

The Temperature Dependence of K

In Chapter 13 we used Le Châtelier's principle to predict qualitatively how the value of K for a given reaction would change with a change in temperature. Now we can specify the quantitative dependence of the equilibrium constant on temperature from the relationship

$$\Delta G^\circ = -RT \ln(K) = \Delta H^\circ - T\Delta S^\circ$$

We can rearrange this equation to give

$$\ln(K) = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T} \right) + \frac{\Delta S^\circ}{R}$$

Note that this is a linear equation of the form $y = mx + b$, where $y = \ln(K)$, $m = -\Delta H^\circ/R = \text{slope}$, $x = 1/T$, and $b = \Delta S^\circ/R = \text{intercept}$. This means that if values of K for a given reaction are determined at various temperatures, a plot of $\ln(K)$ versus $1/T$ will be linear, with slope $-\Delta H^\circ/R$ and intercept $\Delta S^\circ/R$. This result assumes that both ΔH° and ΔS° are independent of temperature over the temperature range considered. This assumption is a good approximation over a relatively small temperature range.

16.9 Free Energy and Work

One of the main reasons we are interested in physical and chemical processes is that we want to use them to do work for us, and we want this work done as efficiently and economically as possible. We have already seen that at constant temperature and pressure, the sign of the change in free energy tells us whether a given process is spontaneous. This is very useful information because it prevents us from wasting effort on a process that has no inherent tendency to occur. Although a thermodynamically favorable chemical reaction may not occur to any appreciable extent because it is too slow, it makes sense in this case to try to find a catalyst to speed up the reaction. On the other hand, if the reaction is prevented from occurring by its thermodynamic characteristics, we would be wasting our time looking for a catalyst.

In addition to its qualitative usefulness (telling us whether a process is spontaneous), the change in free energy is important quantitatively because it can tell us how much work can be done with a given process. In fact, the *maximum possible useful work obtainable from a process at constant temperature and pressure is equal to the change in free energy*:

$$w_{\max} = \Delta G$$

Note that “PV work” is not counted as useful work here.

This relationship explains why this function is called the *free* energy. Under certain conditions, ΔG for a spontaneous process represents the energy that is *free to do useful work*. On the other hand, for a process that is not spontaneous, the value of ΔG tells us the minimum amount of work that must be *expended* to make the process occur.

Knowing the value of ΔG for a process thus gives us valuable information about how close the process is to 100% efficiency. For example, when gasoline is burned in a car’s engine, the work produced is about 20% of the maximum work available.

For reasons we will only briefly introduce in this book, the amount of work we actually obtain from a spontaneous process is *always* less than the maximum possible amount.

To explore this idea more fully, let’s consider an electric current flowing through the starter motor of a car. The current is generated from a chemical change in a battery, and we can calculate ΔG for the battery reaction and so determine the energy available to do work. Can we use all this energy to do work? No, because a current flowing through a wire causes frictional heating, and the greater the current, the greater the heat. This heat represents wasted energy—it is not useful for running the starter motor. We can minimize this energy waste by running very low currents through the motor circuit. However, zero current flow would be necessary to eliminate frictional heating entirely, and we cannot derive any work from the motor if no current flows. This represents the difficulty in which nature places us. Using a process to do work requires that some of the energy be wasted, and usually the faster we run the process, the more energy we waste.

Achieving the maximum work available from a spontaneous process can occur only via a hypothetical pathway. Any real pathway wastes energy. If we could discharge the battery infinitely slowly by an infinitesimal current flow, we would achieve the maximum useful work. Also, if we could then recharge the battery using an infinitesimally small current, exactly the same amount of energy would be used to return the battery to its original state. After we cycle the battery in this way, the universe (the system and surroundings) is exactly the same as it was before the cyclic process. This is a **reversible process** (see Fig. 16.10).

However, if the battery is discharged to run the starter motor and then recharged using a *finite* current flow, as is the case in reality, *more* work will always be required

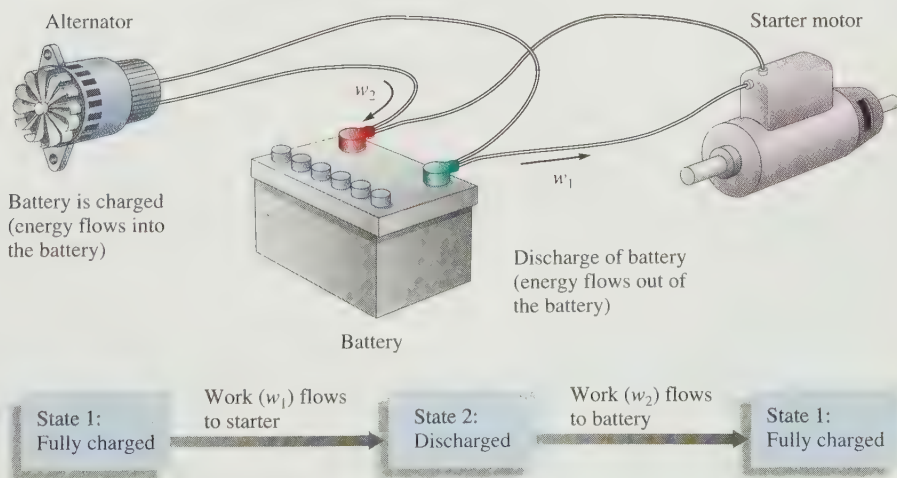


FIGURE 16.10

A battery can do work by sending current to a starter motor. The battery can then be recharged by forcing current through it in the opposite direction. If the current flow in both processes is infinitesimally small, $w_1 = w_2$. This is a *reversible process*. But if the current flow is finite, as it would be in any real case, $w_2 > w_1$. This is an *irreversible process* (the universe is different after the cyclic process occurs). All real processes are irreversible.

to recharge the battery than the battery produces as it discharges. This means that even though the battery (the system) has returned to its original state, the surroundings have not, because the surroundings had to furnish a net amount of work as the battery was cycled. The *universe is different* after this cyclic process is performed, and this function is called an **irreversible process**. *All real processes are irreversible.*

In general, after any real cyclic process is carried out in a system, the surroundings have less ability to do work and contain more thermal energy. In other words, *in any real cyclic process in the system, work is changed to heat in the surroundings, and the entropy of the universe increases*. This is another way of stating the second law of thermodynamics.

Thus thermodynamics tells us the work potential of a process and then tells us that we can never achieve this potential. In this spirit, thermodynamicist Henry Bent has paraphrased the first two laws of thermodynamics as follows:

First law: You can't win, you can only break even.

Second law: You can't break even.

The ideas we have discussed in this section are applicable to the energy crisis that will probably increase in severity over the next 25 years. The crisis is obviously not one of supply; the first law tells us that the universe contains a constant supply of energy. The problem is the availability of *useful* energy. *As we use energy, we degrade its usefulness.* For example, when gasoline reacts with oxygen in the combustion reaction, the change in potential energy results in heat flow. Thus the energy concentrated in the bonds of the gasoline and oxygen molecules ends up *spread* over the surroundings as thermal energy, where it is much more difficult to harness for useful work. This is a way in which the entropy of the universe increases: Concentrated energy becomes spread out—more disordered and less useful. Thus the crux of the energy problem is that we are rapidly consuming the concentrated energy found in fossil fuels. It took millions of years to concentrate the sun's energy in these fuels, and we will consume these same fuels in a few hundred years. Thus we must use these energy sources as wisely as possible.

When energy is used to do work, it becomes less organized and less concentrated and thus less useful.

For Review

Summary

The first law of thermodynamics, which states that the energy of the universe is constant, gives us no clue as to why a particular process occurs in a given direction. A process is said to be spontaneous if it occurs without outside intervention. The driving force for a spontaneous process is described in terms of entropy (S). Entropy is a thermodynamic function that can be viewed as a measure of randomness, or disorder. It describes the number of arrangements (positions and/or energy levels) available to a system existing in a given state. Nature spontaneously proceeds toward states that have the highest probabilities of occurring. The second law of thermodynamics states that for any spontaneous process there is always an increase in the entropy of the universe. Using entropy, thermodynamics predicts the direction in which a process will occur. However, it cannot predict the rate at which the process will occur; this must be done using the principles of kinetics.

Key Terms

Section 16.1

spontaneous process
entropy
positional probability

Section 16.2

second law of thermodynamics

Section 16.4

free energy

Section 16.5

third law of thermodynamics

Section 16.6

standard free energy change

standard free energy of formation

Section 16.8

equilibrium point (thermodynamic definition)

Section 16.9

reversible process

irreversible process

We can predict whether a process is spontaneous by considering the entropy changes that occur in the system and the surroundings:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

For a process at constant temperature and pressure, ΔS_{sys} is dominated by changes in positional entropy, and ΔS_{surr} is determined by heat flow:

$$\Delta S_{\text{surr}} = -\frac{\Delta H}{T}$$

The sign of ΔS_{surr} depends on the direction of the heat flow: ΔS_{surr} is positive for an exothermic process and negative for an endothermic process. The magnitude of ΔS_{surr} , however, depends on both the quantity of energy that flows as heat and the temperature at which the energy is transferred. Thus the significance of exothermicity as a driving force for a process depends on the temperature at which the process occurs.

For a chemical reaction, entropy changes in the system are dominated by the change in the number of gaseous molecules. Fewer gaseous molecules on the product side means a decrease in entropy, and vice versa. Molecular structure also plays a role. In general, a complex molecule has a higher standard entropy than a simpler one.

The third law of thermodynamics states that the entropy of a perfect crystal at 0 K is zero. Above this temperature the molecules will begin to vibrate, and disorder will occur.

Free energy (G) is a thermodynamic function defined by the relationship

$$G = H - TS$$

A process occurring at constant temperature and pressure is spontaneous in the direction in which the free energy decreases.

The standard free energy change (ΔG°) is the change in free energy that will occur if the reactants in their standard states are converted to the products in their standard states. Since free energy is a state function, we can use procedures similar to those used with Hess's law to calculate ΔG° , for example,

$$\Delta G^\circ = \sum n_p \Delta G_f^\circ (\text{products}) - \sum n_r \Delta G_f^\circ (\text{reactants})$$

where ΔG_f° , the standard free energy of formation of a substance, is the change in free energy accompanying the formation of one mole of that substance from its constituent elements with all reactants and products in their standard states. The standard free energy of formation of an element in its standard state is zero.

Free energy depends on pressure according to the equation

$$G = G^\circ + RT \ln(P)$$

The ΔG value for a reaction at conditions other than standard conditions can be calculated from

$$\Delta G = \Delta G^\circ + RT \ln(Q)$$

where Q is the reaction quotient.

The equilibrium position for a chemical reaction occurs where the free energy is the minimum value available to the system. The relationship between ΔG° and the equilibrium constant K is

$$\Delta G^\circ = -RT \ln(K)$$

When ΔG° is equal to zero, the system is at equilibrium with the products and reactants in their standard states ($K = 1$). When ΔG° is less than zero, then $G_{\text{products}}^\circ$ is less than $G_{\text{reactants}}^\circ$, and the system will adjust to the right from standard conditions to attain equilibrium (K is greater than 1). When ΔG° is greater than zero, $G_{\text{reactants}}^\circ$ is less than $G_{\text{products}}^\circ$, and the system will shift to the left from standard conditions to attain equilibrium (K is less than 1).

The maximum possible useful work obtainable from a process at constant temperature and pressure is equal to the change in free energy:

$$w_{\text{max}} = \Delta G$$

In any real process, the actual work obtained is less than w_{max} . When energy is used to do work, the total energy of the universe remains constant, but it is rendered less useful. After being used to do work, concentrated energy is spread out in the surroundings as thermal energy, and this is the crux of our energy problem.

In-Class Discussion Questions

These questions are designed to be considered by groups of students in class. Often these questions work well for introducing a particular topic in class.

1. For the process $A(l) \rightarrow A(g)$, which direction is favored by energy randomness? positional randomness? Explain your answers. If you wanted to favor the process as written, would you raise or lower the temperature of the system? Explain.
2. For a liquid, which would you expect to be larger, ΔS_{fusion} or $\Delta S_{\text{evaporation}}$? Why?
3. Gas A_2 reacts with gas B_2 to form gas AB at a constant temperature. The bond energy of AB is much greater than that of either reactant. What can be said about the sign of ΔH ? ΔS_{sur} ? ΔS ? Explain how potential energy changes for this process. Explain how random kinetic energy changes during the process.
4. What types of experiments can be carried out to determine if a reaction is spontaneous? Does spontaneity have any relationship to the final equilibrium position of a reaction? Explain.
5. A friend tells you, "Free energy G and pressure P are related by the equation $G = G^\circ + RT \ln(P)$. Also, G is related to the equilibrium constant K in that when $G_{\text{products}} = G_{\text{reactants}}$, the system is at equilibrium. Therefore, it must be true that a system is at equilibrium when all the pressures are equal." Do you agree with this friend? Explain.
6. You remember that ΔG° is related to $RT \ln(K)$ but cannot remember if it's $RT \ln(K)$ or $-RT \ln(K)$. Realizing what ΔG° and K mean, how can you figure out the correct sign?

A blue question or exercise number indicates that the answer to that question or exercise appears at the back of this book and a solution appears in the *Solutions Guide*.

Questions

7. Define the following:
 - a. spontaneous process
 - b. entropy
 - c. system
 - d. surroundings
8. Describe how the following changes affect the positional entropy of a substance.
 - a. increase in volume of a gas at constant T
 - b. increase in temperature of a gas at constant V
 - c. increase in pressure of a gas at constant T
9. The synthesis of glucose directly from CO_2 and H_2O and the synthesis of proteins directly from amino acids are both non-spontaneous processes under standard conditions. Yet it is necessary for these to occur for life to exist. In light of the second law of thermodynamics, how can life exist?
10. If you calculate a value for ΔG° for a reaction using the values of ΔG_f° in Appendix 4 and get a negative number, is it correct to say that the reaction is always spontaneous?
11. When the environment is contaminated by a toxic or potentially toxic substance (for example, from a chemical spill or the use of insecticides), the substance tends to disperse. How is this consistent with the second law of thermodynamics? In terms of the second law, which requires the least work: cleaning the environment after it has been contaminated or trying to prevent the contamination before it occurs? Explain.
12. Of the functions ΔH , ΔS , and ΔG , which has the strongest dependence on temperature?
13. Discuss the relationship between w_{max} and the magnitude and sign of the free energy change for a reaction. Also discuss w_{max} for real processes.
14. High temperatures are favorable to a reaction kinetically but may be unfavorable to a reaction thermodynamically. Explain.

Exercises

In this section similar exercises are paired.

Spontaneity, Entropy, and the Second Law of Thermodynamics: Free Energy

15. Which of the following processes are spontaneous?
- Salt dissolves in H_2O .
 - A clear solution becomes a uniform color after a few drops of dye are added.
 - Iron rusts.
 - You clean your bedroom.
16. Which of the following processes are spontaneous?
- A house is built.
 - A satellite is launched into orbit.
 - A satellite falls back to earth.
 - The kitchen gets cluttered.

17. Consider the following energy levels, each capable of holding two objects:

$$E = 2 \text{ kJ} \quad \underline{\hspace{1cm}}$$

$$E = 1 \text{ kJ} \quad \underline{\hspace{1cm}}$$

$$E = 0 \quad \underline{XX}$$

Draw all the possible arrangements of the two identical particles (represented by X) in the three energy levels. What total energy is most likely, that is, occurs the greatest number of times? Assume that the particles are indistinguishable from each other.

18. Redo Exercise 17 with two particles A and B, which can be distinguished from each other.
19. Choose the compound with the greatest positional entropy in each case.
- 1 mol H_2 (at STP) or 1 mol H_2 (at 100°C , 0.5 atm)
 - 1 mol N_2 (at STP) or 1 mol N_2 (at 100 K, 2.0 atm)
 - 1 mol $\text{H}_2\text{O}(s)$ (at 0°C) or 1 mol $\text{H}_2\text{O}(l)$ (at 20°C)

20. Which of the following involve an increase in the entropy of the system?
- melting of a solid
 - sublimation
 - freezing
 - mixing
 - separation
 - boiling

21. Predict the sign of ΔS_{surr} for the following processes.

- $\text{H}_2\text{O}(l) \longrightarrow \text{H}_2\text{O}(g)$
- $\text{CO}_2(g) \longrightarrow \text{CO}_2(s)$

22. Calculate ΔS_{surr} for the following reactions at 25°C and 1 atm.

- $\text{C}_3\text{H}_8(g) + 5\text{O}_2(g) \longrightarrow 3\text{CO}_2(g) + 4\text{H}_2\text{O}(l)$
 $\Delta H^\circ = -2221 \text{ kJ}$
- $2\text{NO}_2(g) \longrightarrow 2\text{NO}(g) + \text{O}_2(g)$
 $\Delta H^\circ = 112 \text{ kJ}$

23. Given the values of ΔH and ΔS , which of the following changes will be spontaneous at constant T and P ?

- $\Delta H = +25 \text{ kJ}$, $\Delta S = +5.0 \text{ J/K}$, $T = 300. \text{ K}$
- $\Delta H = +25 \text{ kJ}$, $\Delta S = +100. \text{ J/K}$, $T = 300. \text{ K}$
- $\Delta H = -10. \text{ kJ}$, $\Delta S = +5.0 \text{ J/K}$, $T = 298 \text{ K}$
- $\Delta H = -10. \text{ kJ}$, $\Delta S = -40. \text{ J/K}$, $T = 200. \text{ K}$

24. At what temperatures will the following processes be spontaneous?

- $\Delta H = -18 \text{ kJ}$ and $\Delta S = -60. \text{ J/K}$
- $\Delta H = +18 \text{ kJ}$ and $\Delta S = +60. \text{ J/K}$
- $\Delta H = +18 \text{ kJ}$ and $\Delta S = -60. \text{ J/K}$
- $\Delta H = -18 \text{ kJ}$ and $\Delta S = +60. \text{ J/K}$

25. Ethanethiol ($\text{C}_2\text{H}_5\text{SH}$; also called ethyl mercaptan) is commonly added to natural gas to provide the “rotten egg” smell of a gas leak. The boiling point of ethanethiol is 35°C and its heat of vaporization is 27.5 kJ/mol . What is the entropy of vaporization for this substance?

26. For mercury, the enthalpy of vaporization is 58.51 kJ/mol and the entropy of vaporization is $92.92 \text{ J/K} \cdot \text{mol}$. What is the normal boiling point of mercury?

27. For ammonia (NH_3), the enthalpy of fusion is 5.65 kJ/mol and the entropy of fusion is $28.9 \text{ J/K} \cdot \text{mol}$.

- Will $\text{NH}_3(s)$ spontaneously melt at $200. \text{ K}$?
- What is the approximate melting point of ammonia?

28. The melting point of tungsten is the second highest among the elements (only that of carbon is higher). The melting point of tungsten is 3680 K , and the enthalpy of fusion is 35.2 kJ/mol . What is the entropy of fusion?

Chemical Reactions: Entropy Changes and Free Energy

29. Predict the sign of ΔS° for each of the following changes.
-



- $\text{AgCl}(s) \longrightarrow \text{Ag}^+(aq) + \text{Cl}^-(aq)$
- $2\text{H}_2(g) + \text{O}_2(g) \longrightarrow 2\text{H}_2\text{O}(l)$
- $\text{H}_2\text{O}(l) \longrightarrow \text{H}_2\text{O}(g)$

30. Predict the sign of ΔS° for each of the following changes.

- $\text{Na}(s) + \frac{1}{2}\text{Cl}_2(g) \longrightarrow \text{NaCl}(s)$
- $\text{N}_2(g) + 3\text{H}_2(g) \longrightarrow 2\text{NH}_3(g)$
- $\text{NaCl}(s) \longrightarrow \text{Na}^+(aq) + \text{Cl}^-(aq)$
- $\text{NaCl}(s) \longrightarrow \text{NaCl}(l)$

31. For each of the following pairs of substances, which substance has the greater value of S at 25°C ?

- $\text{C}_{\text{graphite}}(s)$ or $\text{C}_{\text{diamond}}(s)$
- $\text{C}_2\text{H}_5\text{OH}(l)$ or $\text{C}_2\text{H}_5\text{OH}(g)$
- $\text{CO}_2(s)$ or $\text{CO}_2(g)$

32. For each of the following pairs, which substance has the greater value of S° ?

- N_2O (at 0 K) or He (at 10 K)
- $\text{N}_2\text{O(g)}$ (at 1 atm, 25°C) or He(g) (at 1 atm, 25°C)
- $\text{H}_2\text{O(s)}$ (at 0°C) or $\text{H}_2\text{O(l)}$ (at 0°C)

33. Predict the sign of ΔS° and then calculate ΔS° for each of the following reactions.

- $2\text{H}_2\text{S(g)} + \text{SO}_2\text{(g)} \longrightarrow 3\text{S}_{\text{rhombic}}\text{(s)} + 2\text{H}_2\text{O(g)}$
- $2\text{SO}_3\text{(g)} \longrightarrow 2\text{SO}_2\text{(g)} + \text{O}_2\text{(g)}$
- $\text{Fe}_2\text{O}_3\text{(s)} + 3\text{H}_2\text{(g)} \longrightarrow 2\text{Fe(s)} + 3\text{H}_2\text{O(g)}$

34. Predict the sign of ΔS° and then calculate ΔS° for each of the following reactions.

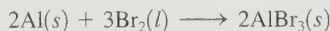
- $\text{H}_2\text{(g)} + \frac{1}{2}\text{O}_2\text{(g)} \longrightarrow \text{H}_2\text{O(l)}$
- $\text{N}_2\text{(g)} + 3\text{H}_2\text{(g)} \longrightarrow 2\text{NH}_3\text{(g)}$
- $\text{HCl(g)} \longrightarrow \text{H}^+\text{(aq)} + \text{Cl}^-\text{(aq)}$

35. For the reaction



ΔS° is equal to -358 J/K . Use this value and data from Appendix 4 to calculate the value of S° for $\text{CF}_4\text{(g)}$.

36. For the reaction



ΔS° is equal to -144 J/K . Use this value and data from Appendix 4 to calculate the value of S° for solid aluminum bromide.

37. It is quite common for a solid to change from one structure to another at a temperature below its melting point. For example, sulfur undergoes a phase change from the rhombic crystal structure to the monoclinic crystal form at temperatures above 95°C .

- Predict the signs of ΔH and ΔS for the process $\text{S}_{\text{rhombic}} \longrightarrow \text{S}_{\text{monoclinic}}$.
- Which form of sulfur has the more ordered crystalline structure?

38. When most biologic enzymes are heated they lose their catalytic activity. The change



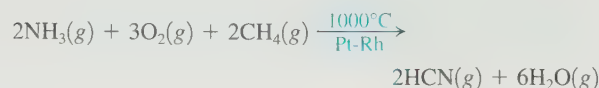
that occurs on heating is endothermic and spontaneous. Is the structure of the original enzyme or its new form more ordered? Explain.

39. Consider the reaction



- Predict the signs of ΔH and ΔS .
- Would the reaction be more spontaneous at high or low temperatures?

40. Hydrogen cyanide is produced industrially by the following exothermic reaction:



Is the high temperature needed for thermodynamic or kinetic reasons?

41. From data in Appendix 4, calculate ΔH° , ΔS° , and ΔG° for each of the following reactions at 25°C .

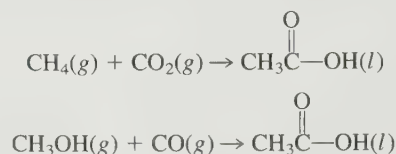
- $\text{CH}_4\text{(g)} + 2\text{O}_2\text{(g)} \longrightarrow \text{CO}_2\text{(g)} + 2\text{H}_2\text{O(g)}$
- $6\text{CO}_2\text{(g)} + 6\text{H}_2\text{O(l)} \longrightarrow \text{C}_6\text{H}_{12}\text{O}_6\text{(s)} + 6\text{O}_2\text{(g)}$
Glucose
- $\text{P}_4\text{O}_{10}\text{(s)} + 6\text{H}_2\text{O(l)} \longrightarrow 4\text{H}_3\text{PO}_4\text{(s)}$
- $\text{HCl(g)} + \text{NH}_3\text{(g)} \longrightarrow \text{NH}_4\text{Cl(s)}$

42. For the reaction at 298 K,



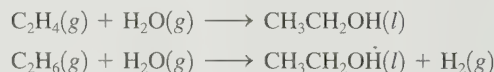
the values of ΔH° and ΔS° are -58.03 kJ and -176.6 J/K , respectively. What is the value of ΔG° at 298 K? Assuming that ΔH° and ΔS° do not depend on temperature, at what temperature is $\Delta G^\circ = 0$? Is ΔG° negative above or below this temperature?

43. Using data from Appendix 4, calculate ΔH° , ΔS° , and ΔG° for the following reactions that produce acetic acid:



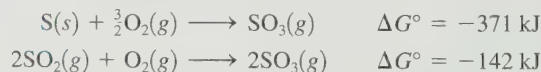
Which reaction would you choose as a commercial method for producing acetic acid ($\text{CH}_3\text{CO}_2\text{H}$) at standard conditions? What temperature conditions would you choose for the reaction? Assume ΔH° and ΔS° do not depend on temperature.

44. Consider two reactions for the production of ethanol:

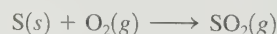


Which would be the more thermodynamically feasible at standard conditions? Why?

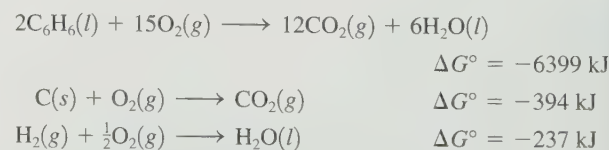
45. Given the following data



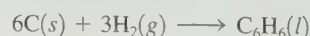
calculate ΔG° for the reaction



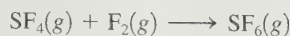
46. Given the following data:



calculate ΔG° for the reaction



47. For the reaction



the value of ΔG° is -374 kJ. Use this value and data from Appendix 4 to calculate the value of ΔG_f° for $\text{SF}_4(g)$.

48. The value of ΔG° for the reaction



is -5490 kJ. Use this value and data from Appendix 4 to calculate the standard free energy of formation for $\text{C}_4\text{H}_{10}(g)$.

49. Use the ΔG_f° values in Appendix 4 to calculate ΔG° for the reaction



50. Consider the reaction



- Calculate ΔG° for this reaction. The ΔG_f° values for $\text{POCl}_3(g)$ and $\text{PCl}_3(g)$ are -502 kJ/mol and -270 kJ/mol, respectively.
- Is this reaction spontaneous under standard conditions at 298 K?
- The value of ΔS° for this reaction is 179 J/K. At what temperatures is this reaction spontaneous at standard conditions? Assume that ΔH° and ΔS° do not depend on temperature.

Free Energy: Pressure Dependence and Equilibrium

51. Using data from Appendix 4, calculate ΔG for the reaction



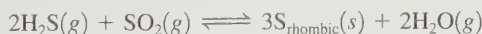
for these conditions:

$$T = 298 \text{ K}$$

$$P_{\text{NO}} = 1.00 \times 10^{-6} \text{ atm}, P_{\text{O}_3} = 2.00 \times 10^{-6} \text{ atm}$$

$$P_{\text{NO}_2} = 1.00 \times 10^{-7} \text{ atm}, P_{\text{O}_2} = 1.00 \times 10^{-3} \text{ atm}$$

52. Using data from Appendix 4, calculate ΔG for the reaction



for the following conditions at 25°C :

$$P_{\text{H}_2\text{S}} = 1.0 \times 10^{-4} \text{ atm}$$

$$P_{\text{SO}_2} = 1.0 \times 10^{-2} \text{ atm}$$

$$P_{\text{H}_2\text{O}} = 3.0 \times 10^{-2} \text{ atm}$$

53. Consider the reaction



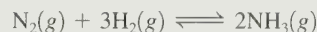
For each of the following mixtures of reactants and products at 25°C , predict the direction in which the reaction will shift to reach equilibrium.

$$\text{a. } P_{\text{NO}_2} = P_{\text{N}_2\text{O}_4} = 1.0 \text{ atm}$$

$$\text{b. } P_{\text{NO}_2} = 0.21 \text{ atm}, P_{\text{N}_2\text{O}_4} = 0.50 \text{ atm}$$

$$\text{c. } P_{\text{NO}_2} = 0.29 \text{ atm}, P_{\text{N}_2\text{O}_4} = 1.6 \text{ atm}$$

54. Using data from Appendix 4, calculate ΔH° , ΔS° , and K (at 298 K) for the synthesis of ammonia by the Haber process:



Calculate ΔG for this reaction under the following conditions (assume an uncertainty of ± 1 in all quantities):

$$\text{a. } T = 298 \text{ K}, P_{\text{N}_2} = P_{\text{H}_2} = 200 \text{ atm}, P_{\text{NH}_3} = 50 \text{ atm}$$

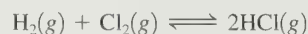
$$\text{b. } T = 298 \text{ K}, P_{\text{N}_2} = 200 \text{ atm}, P_{\text{H}_2} = 600 \text{ atm}, P_{\text{NH}_3} = 200 \text{ atm}$$

55. Consider the following reaction at 25.0°C :



The values of ΔH° and ΔS° are -58.03 kJ/mol and -176.6 J/K $\cdot$ mol, respectively. Calculate the value of K at 25.0°C . Assuming ΔH° and ΔS° are temperature independent, estimate the value of K at 100.0°C .

56. Consider the reaction



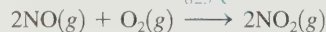
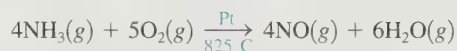
- Calculate ΔH° , ΔS° , ΔG° , and K (at 298 K) using data in Appendix 4.
- If $\text{H}_2(g)$, $\text{Cl}_2(g)$, and $\text{HCl}(g)$ are placed in a flask such that the pressure of each gas is 1 atm, in which direction will the system shift to reach equilibrium at 25°C ?

57. Consider the autoionization of water at 25°C :



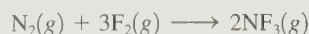
- Calculate ΔG° for this process at 25°C .
- At $40.^\circ\text{C}$, $K_w = 2.92 \times 10^{-14}$. Calculate ΔG° at $40.^\circ\text{C}$.

58. The Ostwald process for the commercial production of nitric acid involves three steps:



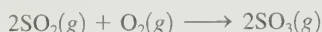
- Calculate ΔH° , ΔS° , ΔG° , and K (at 298 K) for each of the three steps in the Ostwald process (see Appendix 4).
- Calculate the equilibrium constant for the first step at 825°C , assuming ΔH° and ΔS° do not depend on temperature.
- Is there a thermodynamic reason for the high temperature in the first step assuming standard conditions?

59. Consider the following reaction at $800.$ K:



An equilibrium mixture contains the following partial pressures: $P_{\text{N}_2} = 0.021$ atm, $P_{\text{F}_2} = 0.063$ atm, $P_{\text{NF}_3} = 0.48$ atm. Calculate ΔG° for the reaction at $800.$ K.

60. Consider the following reaction at 298 K:

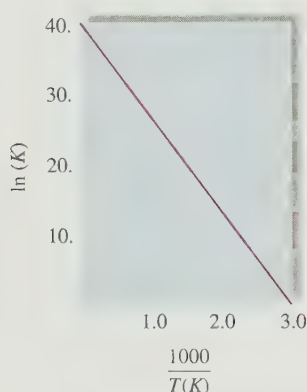


An equilibrium mixture contains $\text{O}_2(g)$ and $\text{SO}_3(g)$ at partial pressures of 0.50 atm and 2.0 atm, respectively. Using data from Appendix 4, determine the equilibrium partial pressure of SO_2 in the mixture. Will this reaction be most favored at a high or a low temperature, assuming standard conditions?

61. Consider the relationship:

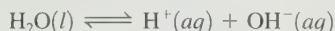
$$\ln(K) = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

The equilibrium constant for some hypothetical process was determined as a function of temperature (in Kelvin) with the results plotted below.



From the plot, determine the values of ΔH° and ΔS° for this process. What would be the major difference in the $\ln(K)$ versus $1/T$ plot for an endothermic process as compared to an exothermic process?

62. Use the equation in Exercise 61 to determine
- ΔH°
- and
- ΔS°
- for the autoionization of water:



$T(^{\circ}\text{C})$	K_w
0	1.14×10^{-15}
25	1.00×10^{-14}
35	2.09×10^{-14}
40	2.92×10^{-14}
50	5.47×10^{-14}

Animals use glucose as a source of energy:



If we were to assume that both these processes occur to the same extent in a cyclic process, what thermodynamic property must have a nonzero value?

64. Some water is placed in a coffee-cup calorimeter. When 1.0 g of an ionic solid is added, the temperature of the solution increases from 21.5°C to 24.2°C as the solid dissolves. For the dissolving process, what are the signs for ΔS_{sys} , ΔS_{surr} , and ΔS_{univ} ?
65. Human DNA contains almost twice as much information as is needed to code for all the substances produced in the body. Likewise, the digital data sent from *Voyager II* contained one redundant bit out of every two bits of information. The Hubble space telescope transmits three redundant bits for every bit of information. How is entropy related to the transmission of information? What do you think is accomplished by having so many redundant bits of information in both DNA and the space probes?
66. Calculate the entropy change for the vaporization of liquid methane and liquid hexane using the following data.

	Boiling Point (1 atm)	ΔH_{vap}
Methane	112 K	8.20 kJ/mol
Hexane	342 K	28.9 kJ/mol

Compare the molar volume of gaseous methane at 112 K with that of gaseous hexane at 342 K. How do the differences in molar volume affect the values of ΔS_{vap} for these liquids?

67. Elemental sulfur can exist in two crystalline forms, rhombic and monoclinic. Calculate the temperature for the conversion of monoclinic sulfur to rhombic sulfur given the following data:

	ΔH_f° (kJ/mol)	S° (J/K · mol)
S (rhombic)	0	31.73
S (monoclinic)	0.30	32.55

68. Consider the following reaction:



For $\text{Cl}_2\text{O}(g)$,

$$\Delta G_f^\circ = 97.9 \text{ kJ/mol}$$

$$\Delta H_f^\circ = 80.3 \text{ kJ/mol}$$

$$S^\circ = 266.1 \text{ J/K} \cdot \text{mol}$$

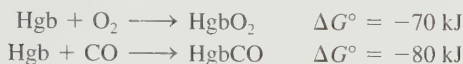
- a. Calculate ΔG° for the reaction using the equation $\Delta G^\circ = -RT \ln(K)$.
- b. Use bond energy values (Table 8.4) to estimate ΔH° for the reaction.

Additional Exercises

63. A green plant synthesizes glucose by photosynthesis, as shown in the reaction



- c. Use the results from parts a and b to estimate ΔS° for the reaction.
 - d. Estimate ΔH_f° and S° for HOCl(g) .
 - e. Estimate the value of K at 500. K.
 - f. Calculate ΔG at 25°C when $P_{\text{H}_2\text{O}} = 18$ torr, $P_{\text{Cl}_2\text{O}} = 2.0$ torr, and $P_{\text{HOCl}} = 0.10$ torr.
69. Carbon monoxide is toxic because it bonds much more strongly to the iron in hemoglobin (Hgb) than does O_2 . Consider the following reactions and approximate standard free energy changes:



Using these data, estimate the equilibrium constant value at 25°C for the following reaction:



70. Using the following data, calculate the value of K_{sp} for $\text{Ba}(\text{NO}_3)_2$, one of the *least* soluble of the common nitrate salts.

Species	ΔG_f°
$\text{Ba}^{2+}(aq)$	-561 kJ/mol
$\text{NO}_3^-(aq)$	-109 kJ/mol
$\text{Ba}(\text{NO}_3)_2(s)$	-797 kJ/mol

- 71.** In the text the following equation was derived

$$\Delta G = \Delta G^\circ + RT \ln(Q)$$

for gaseous reactions where the quantities in Q were expressed in units of pressure. We also can use units of mol/L for the quantities in Q , specifically for aqueous reactions. With this in mind, consider the reaction



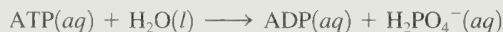
for which $K_a = 7.2 \times 10^{-4}$ at 25°C . Calculate ΔG for the reaction under the following conditions at 25°C .

- a. $[\text{HF}] = [\text{H}^+] = [\text{F}^-] = 1.0\text{ M}$
b. $[\text{HF}] = 0.98\text{ M}$, $[\text{H}^+] = [\text{F}^-] = 2.7 \times 10^{-2}\text{ M}$
c. $[\text{HF}] = [\text{H}^+] = [\text{F}^-] = 1.0 \times 10^{-5}\text{ M}$
d. $[\text{HF}] = [\text{F}^-] = 0.27\text{ M}$, $[\text{H}^+] = 7.2 \times 10^{-4}\text{ M}$
e. $[\text{HF}] = 0.52\text{ M}$, $[\text{F}^-] = 0.67\text{ M}$, $[\text{H}^+] = 1.0 \times 10^{-3}\text{ M}$
Based on the calculated ΔG values, in what direction will the reaction shift to reach equilibrium for each of the five sets of conditions?

72. Many biochemical reactions that occur in cells require relatively high concentrations of potassium ion (K^+). The concentration of K^+ in muscle cells is about 0.15 M . The concentration of K^+ in blood plasma is about 0.0050 M . The high internal concentration in cells is maintained by pumping K^+ from the plasma. How much work must be done to transport $1.0\text{ mol } K^+$ from the blood to the inside of a muscle cell at 37°C , normal body temperature? When $1.0\text{ mol } K^+$ is trans-

ferred from blood to the cells, do any other ions have to be transported? Why or why not?

73. Cells use the hydrolysis of adenosine triphosphate, abbreviated as ATP, as a source of energy. Symbolically, this reaction can be written as



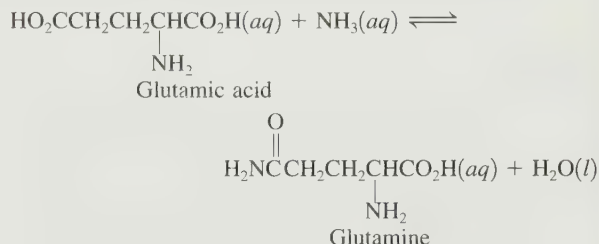
where ADP represents adenosine diphosphate. For this reaction, $\Delta G^\circ = -30.5$ kJ/mol.

- Calculate K at 25°C.
- If all the free energy from the metabolism of glucose



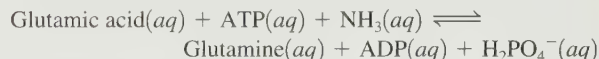
goes into forming ATP from ADP, how many ATP molecules can be produced for every molecule of glucose?

74. One reaction that occurs in human metabolism is

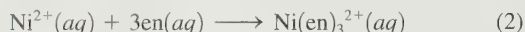
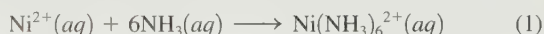


For this reaction $\Delta G^\circ = 14 \text{ kJ}$ at 25°C .

- Calculate K for this reaction at 25°C.
- In a living cell this reaction is coupled with the hydrolysis of ATP. (See Exercise 73.) Calculate ΔG° and K at 25°C for the following reaction:



75. Consider the reactions



where



The ΔH values for the two reactions are quite similar, yet $K_{\text{reaction 2}} > K_{\text{reaction 1}}$. Explain.

76. Consider the reaction



Assuming ΔH° and ΔS° do not depend on temperature, calculate the temperature where $K = 1.00$ for this reaction.

Challenge Problems

77. Using data from Appendix 4, calculate ΔH° , ΔG° , and K (at 298 K) for the production of ozone from oxygen:



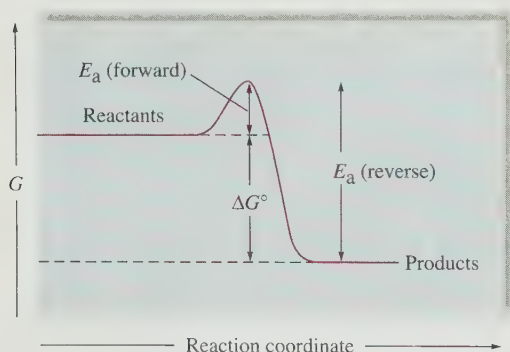
At 30 km above the surface of the earth, the temperature is about 230. K and the partial pressure of oxygen is about 1.0×10^{-3} atm. Estimate the partial pressure of ozone in equilibrium with oxygen at 30 km above the earth's surface. Is it reasonable to assume that the equilibrium between oxygen and ozone is maintained under these conditions? Explain.

78. Entropy can be calculated by a relationship proposed by Ludwig Boltzmann:

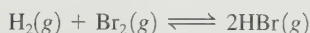
$$S = k \ln(W)$$

where $k = 1.38 \times 10^{-23}$ J/K and W is the number of ways a particular state can be obtained. (This equation is engraved on Boltzmann's tombstone.) Calculate S for the three arrangements of particles in Table 16.1.

79. a. Using the free energy profile for a simple one-step reaction, show that at equilibrium $K = k_f/k_r$, where k_f and k_r are the rate constants for the forward and reverse reactions. Hint: Use the relationship $\Delta G^\circ = -RT \ln(K)$ and represent k_f and k_r using the Arrhenius equation ($k = Ae^{-E_a/RT}$).



- b. Why is the following statement false? "A catalyst can increase the rate of a forward reaction but not the rate of the reverse reaction."
80. Consider the reaction



where $\Delta H^\circ = -103.8$ kJ/mol. In a particular experiment, equal moles of $\text{H}_2(\text{g})$ at 1.00 atm and $\text{Br}_2(\text{g})$ at 1.00 atm were mixed in a 1.00-L flask at 25°C and allowed to reach equilibrium. Then the molecules of H_2 at equilibrium were counted using a very sensitive technique, and 1.10×10^{13} molecules were found. For this reaction, calculate the values of K , ΔG° , and ΔS° .

81. Consider the system



at 25°C .

- a. Assuming that $G_A^\circ = 8996$ J/mol and $G_B^\circ = 11,718$ J/mol, calculate the value of the equilibrium constant for this reaction.

- b. Calculate the equilibrium pressures that result if 1.00 mol $\text{A}(\text{g})$ at 1.00 atm and 1.00 mol $\text{B}(\text{g})$ at 1.00 atm are mixed at 25°C .

- c. Show by calculations that $\Delta G = 0$ at equilibrium.

82. The equilibrium constant for a certain reaction decreases from 8.84 to 3.25×10^{-2} when the temperature increases from 25°C to 75°C . Estimate the temperature where $K = 1.00$ for this reaction. Estimate the value of ΔS° for this reaction. Hint: Manipulate the equation in Exercise 61.

83. If wet silver carbonate is dried in a stream of hot air, the air must have a certain concentration level of carbon dioxide to prevent silver carbonate from decomposing by the reaction



ΔH° for this reaction is 79.14 kJ/mol in the temperature range of 25 to 125°C . Given that the partial pressure of carbon dioxide in equilibrium with pure solid silver carbonate is 6.23×10^{-3} torr at 25°C , calculate the partial pressure of CO_2 necessary to prevent decomposition of Ag_2CO_3 at 110°C . Hint: Manipulate the equation in Exercise 61.

84. Carbon tetrachloride (CCl_4) and benzene (C_6H_6) form ideal solutions. Consider an equimolar solution of CCl_4 and C_6H_6 at 25°C . The vapor above the solution is collected and condensed. Using the following data, determine the composition in mole fraction of the condensed vapor.

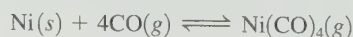
Substance	ΔG_f°
$\text{C}_6\text{H}_6(\text{l})$	124.50 kJ/mol
$\text{C}_6\text{H}_6(\text{g})$	129.66 kJ/mol
$\text{CCl}_4(\text{l})$	-65.21 kJ/mol
$\text{CCl}_4(\text{g})$	-60.59 kJ/mol

85. Some nonelectrolyte solute (molar mass = 142 g/mol) was dissolved in 150. mL of a solvent (density = 0.879 g/cm³). The elevated boiling point of the solution was 355.4 K. What mass of solute was dissolved in the solvent? For the solvent, the enthalpy of vaporization is 33.90 kJ/mol, the entropy of vaporization is 95.95 J/K · mol, and the boiling-point elevation constant is 2.5 K · kg/mol.

Marathon Problem

This problem is designed to incorporate several concepts and techniques into one situation. Marathon Problems can be used in class by groups of students to help facilitate problem-solving skills.

86. Impure nickel, refined by smelting sulfide ores in a blast furnace, can be converted into metal from 99.90% to 99.99% purity by the Mond process. The primary reaction involved in the Mond process is





Media Activities

- a. Without referring to Appendix 4, predict the sign of ΔS° for the above reaction. Explain.
- b. The spontaneity of the above reaction is temperature dependent. Predict the sign of ΔS_{surr} for this reaction. Explain.
- c. For $\text{Ni}(\text{CO})_4(g)$, $\Delta H_f^\circ = -607 \text{ kJ/mol}$ and $S^\circ = 417 \text{ J/K} \cdot \text{mol}$ at 298 K. Using these values and data in Appendix 4, calculate ΔH° and ΔS° for the above reaction.
- d. Calculate the temperature at which $\Delta G^\circ = 0$ ($K = 1$) for the above reaction, assuming that ΔH° and ΔS° do not depend on temperature.
- e. The first step of the Mond process involves equilibrating impure nickel with $\text{CO}(g)$ and $\text{Ni}(\text{CO})_4(g)$ at about 50°C . The purpose of this step is to convert as much nickel as possible into the gas phase. Calculate the equilibrium constant for the above reaction at 50°C .
- f. In the second step of the Mond process, the gaseous $\text{Ni}(\text{CO})_4$ is isolated and heated to 227°C . The purpose of this step is to deposit as much nickel as possible as pure solid (the reverse of the above reaction). Calculate the equilibrium constant for the above reaction at 227°C .
- g. Why is temperature increased for the second step of the Mond process?
- h. The Mond process relies on the volatility of $\text{Ni}(\text{CO})_4$ for its success. Only pressures and temperatures at which $\text{Ni}(\text{CO})_4$ is a gas are useful. A recently developed variation of the Mond process carries out the first step at higher pressures and a temperature of 152°C . Estimate the maximum pressure of $\text{Ni}(\text{CO})_4(g)$ that can be attained before the gas will liquefy at 152°C . The boiling point for $\text{Ni}(\text{CO})_4$ is 42°C and the enthalpy of vaporization is 29.0 kJ/mol . (*Hint:* The phase change reaction and the corresponding equilibrium expression are



$\text{Ni}(\text{CO})_4(g)$ will liquefy when the pressure of $\text{Ni}(\text{CO})_4$ is greater than the K value.)

1. a. Read the overview on the student CD for Chapter 16 to review important topics covered in this chapter. What is the second law of thermodynamics? What determines ΔS_{sys} ? ΔS_{surr} ? Practice predicting signs for ΔS_{sys} and ΔS_{surr} by doing Exercises 16.20, 16.21, and 16.29 in the text.
 - b. How is ΔS_{surr} calculated? Why is the negative sign in the equation? Why is ΔS_{surr} inversely related to temperature?
 - c. To predict spontaneity, ΔS_{sys} and ΔS_{surr} must both be considered. At what values of ΔS_{univ} is a process spontaneous? Under what sign combination of ΔS_{sys} and ΔS_{surr} is a process always spontaneous? Never spontaneous? Sometimes spontaneous? See Table 16.3 in the text to check your answers.
2. Test your understanding of Chapter 16 material by taking the ACE quizzes on the student web site.



For additional web activities and other resources, visit the Zumdahl, *Chemistry*, Sixth Edition textbook site at <http://chemistry.college.hmco.com/students>.



Electrochemistry

17

Electrochemistry constitutes one of the most important interfaces between chemistry and everyday life. Every time you start your car, turn on your calculator, look at your digital watch, or listen to a radio at the beach, you are depending on electrochemical reactions. Our society sometimes seems to run almost entirely on batteries. Certainly the advent of small, dependable batteries along with silicon-chip technology has made possible the tiny calculators, tape recorders, and clocks that we take for granted.

Electrochemistry is important in other less obvious ways. For example, the corrosion of iron, which has tremendous economic implications, is an electrochemical process. In addition, many important industrial materials such as aluminum, chlorine, and sodium hydroxide are prepared by electrolytic processes. In analytical chemistry, electrochemical techniques employ electrodes that are specific for a given molecule or ion, such as H^+ (pH meters), F^- , Cl^- , and many others. These increasingly important methods are used to analyze for trace pollutants in natural waters or for the tiny quantities of chemicals in human blood that may signal the development of a specific disease.

Electrochemistry is best defined as *the study of the interchange of chemical and electrical energy*. It is primarily concerned with two processes that involve oxidation–reduction reactions: the generation of an electric current from a spontaneous chemical reaction and the opposite process, the use of a current to produce chemical change.

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17.2 Standard Reduction Potentials

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- Complete Description of a Galvanic Cell

17.3 Cell Potential, Electrical Work, and Free Energy

17.4 Dependence of Cell Potential on Concentration

- Concentration Cells
- The Nernst Equation
- Ion-Selective Electrodes
- Calculation of Equilibrium Constants for Redox Reactions

17.5 Batteries

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- Metal Plating
- Electrolysis of Sodium Chloride

17.1 Galvanic Cells

Understanding Concepts:
ElectrochemistryBalancing half-reactions is discussed in
Section 4.10.

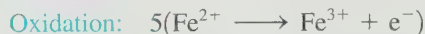
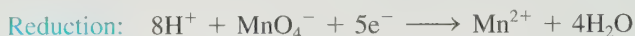
As we discussed in detail in Section 4.9, an **oxidation–reduction (redox) reaction** involves a transfer of electrons from the **reducing agent** to the **oxidizing agent**. Recall that **oxidation** involves a *loss of electrons* (an increase in oxidation number) and that **reduction** involves a *gain of electrons* (a decrease in oxidation number).

To understand how a redox reaction can be used to generate a current, let's consider the reaction between MnO_4^- and Fe^{2+} :



In this reaction, Fe^{2+} is oxidized and MnO_4^- is reduced; electrons are transferred from Fe^{2+} (the reducing agent) to MnO_4^- (the oxidizing agent).

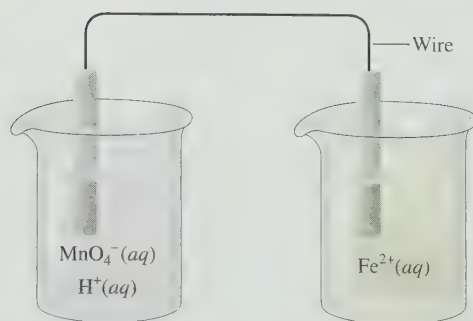
It is useful to break a redox reaction into **half-reactions**, one involving oxidation and one involving reduction. For the reaction above, the half-reactions are



The multiplication of the second half-reaction by 5 indicates that this reaction must occur five times for each time the first reaction occurs. The balanced overall reaction is the sum of the half-reactions.

When MnO_4^- and Fe^{2+} are present in the same solution, the electrons are transferred directly when the reactants collide. Under these conditions, no useful work is obtained from the chemical energy involved in the reaction, which instead is released as heat. How can we harness this energy? The key is to separate the oxidizing agent from the reducing agent, thus requiring the electron transfer to occur through a wire. The current produced in the wire by the electron flow can then be directed through a device, such as an electric motor, to provide useful work.

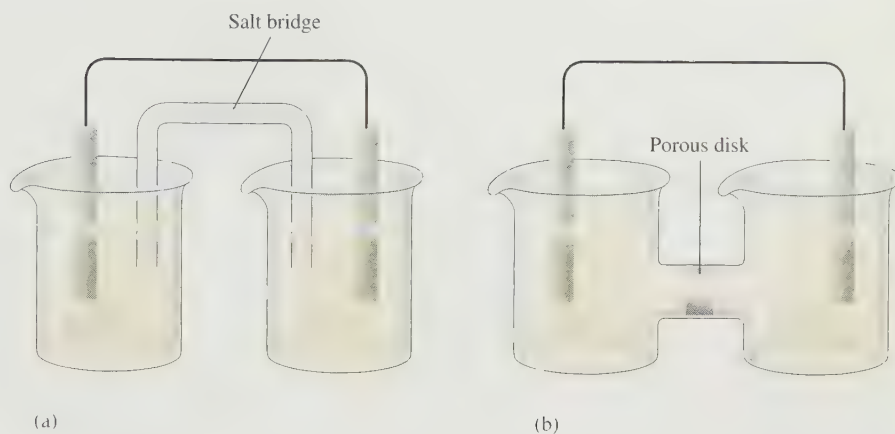
For example, consider the system illustrated in Fig. 17.1. If our reasoning has been correct, electrons should flow through the wire from Fe^{2+} to MnO_4^- . However, when we construct the apparatus as shown, no flow of electrons is apparent. Why? Careful observation shows that when we connect the wires from the two compartments, current flows for an instant and then ceases. The current stops flowing because of charge buildups in the two compartments. If electrons flowed from the right to the left compartment in the apparatus as shown, the left compartment (receiving electrons) would become negatively charged, and the right compartment (losing electrons) would become positively charged. Creating a charge separation of this type requires a large amount of energy. Thus sustained electron flow cannot occur under these conditions.

**FIGURE 17.1**

Schematic of a method to separate the oxidizing and reducing agents of a redox reaction. (The solutions also contain counterions to balance the charge.)

FIGURE 17.2

Galvanic cells can contain a salt bridge as in (a) or a porous-disk connection as in (b). A salt bridge contains a strong electrolyte held in a Jello-like matrix. A porous disk contains tiny passages that allow hindered flow of ions.



A galvanic cell uses a spontaneous redox reaction to produce a current that can be used to do work.

Oxidation occurs at the anode. Reduction occurs at the cathode.

However, we can solve this problem very simply. The solutions must be connected so that ions can flow to keep the net charge in each compartment zero. This connection might involve a **salt bridge** (a U-tube filled with an electrolyte) or a **porous disk** in a tube connecting the two solutions (see Fig. 17.2). Either of these devices allow ions to flow without extensive mixing of the solutions. When we make the provision for ion flow, the circuit is complete. Electrons flow through the wire from reducing agent to oxidizing agent, and ions flow from one compartment to the other to keep the net charge zero.

We now have covered all the essential characteristics of a **galvanic cell**, a device in which chemical energy is changed to electrical energy. (The opposite process is called *electrolysis* and will be considered in Section 17.7.)

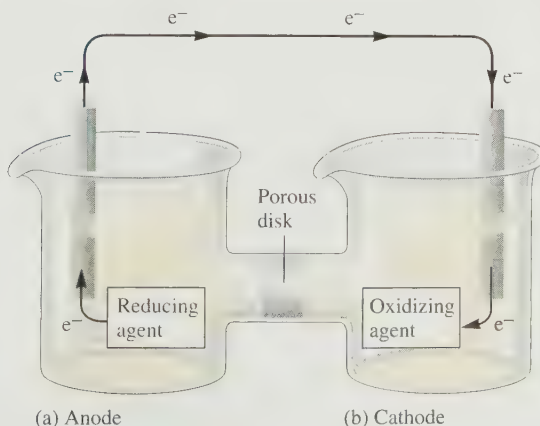
The reaction in an electrochemical cell occurs at the interface between the electrode and the solution where the electron transfer occurs. The electrode compartment in which *oxidation* occurs is called the **anode**; the electrode compartment in which *reduction* occurs is called the **cathode** (see Fig. 17.3).

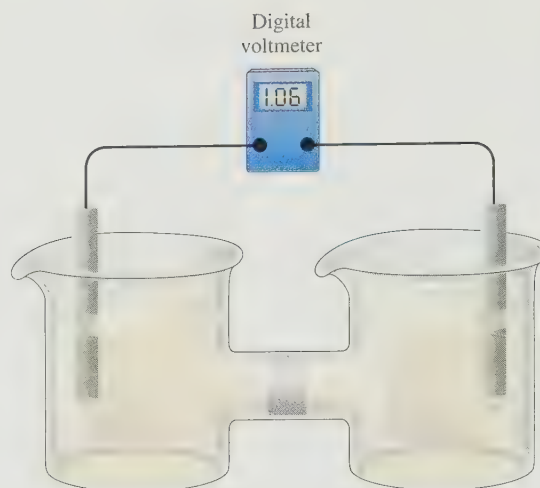
Cell Potential

A galvanic cell consists of an oxidizing agent in one compartment that pulls electrons through a wire from a reducing agent in the other compartment. The “pull,” or driving force, on the electrons is called the **cell potential** ($\mathcal{E}_{\text{cell}}$), or the **electromotive**

FIGURE 17.3

An electrochemical process involves electron transfer at the interface between the electrode and the solution. (a) The species in the solution acting as the reducing agent supplies electrons to the anode. (b) The species in the solution acting as the oxidizing agent receives electrons from the cathode.



**FIGURE 17.4**

Digital voltmeters draw only a negligible current and are convenient to use.

A volt is 1 joule of work per coulomb of charge transferred: $1 \text{ V} = 1 \text{ J/C}$.

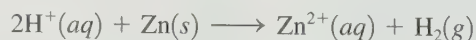
force (emf) of the cell. The unit of electrical potential is the **volt** (abbreviated V), which is defined as 1 joule of work per coulomb of charge transferred.

How can we measure the cell potential? One possible instrument is a crude **voltmeter**, which works by drawing current through a known resistance. However, when current flows through a wire, the frictional heating that occurs wastes some of the potentially useful energy of the cell. A traditional voltmeter will therefore measure a potential that is less than the maximum cell potential. The key to determining the maximum potential is to do the measurement under conditions of zero current so that no energy is wasted. Traditionally, this has been accomplished by inserting a variable-voltage device (powered from an external source) in *opposition* to the cell potential. The voltage on this instrument (called a **potentiometer**) is adjusted until no current flows in the cell circuit. Under such conditions, the cell potential is equal in magnitude and opposite in sign to the voltage setting of the potentiometer. This value represents the *maximum* cell potential, since no energy is wasted heating the wire. More recently, advances in electronic technology have allowed the design of *digital voltmeters* that draw only a negligible amount of current (see Fig. 17.4). Since these instruments are more convenient to use, they have replaced potentiometers in the modern laboratory.

17.2 Standard Reduction Potentials

The name *galvanic cell* honors Luigi Galvani (1737–1798), an Italian scientist generally credited with the discovery of electricity. These cells are sometimes called *voltaic cells* after Alessandro Volta (1745–1827), another Italian, who first constructed cells of this type around 1800.

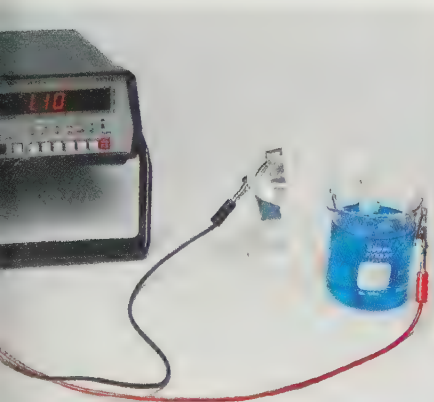
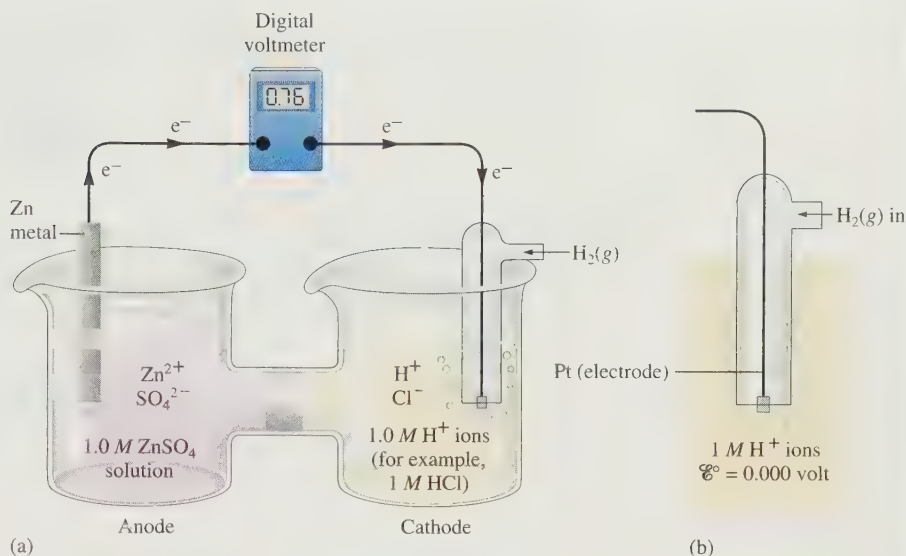
The reaction in a galvanic cell is always an oxidation–reduction reaction that can be broken down into two half-reactions. It would be convenient to assign a potential to *each* half-reaction so that when we construct a cell from a given pair of half-reactions we can obtain the cell potential by summing the half-cell potentials. For example, the observed potential for the cell shown in Fig. 17.5(a) is 0.76 V, and the cell reaction* is



*In this text we will follow the convention of indicating the physical states of the reactants and products only in the overall redox reaction. For simplicity, half-reactions will *not* include the physical states.

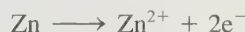
FIGURE 17.5

(a) A galvanic cell involving the reactions $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$ (at the anode) and $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ (at the cathode) has a potential of 0.76 V. (b) The standard hydrogen electrode where $\text{H}_2(\text{g})$ at 1 atm is passed over a platinum electrode in contact with 1 M H^+ ions. This electrode process (assuming ideal behavior) is arbitrarily assigned a value of exactly zero volts.

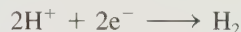


An electrochemical cell with a measured potential of 1.10 V.

For this cell, the anode compartment contains a zinc metal electrode with Zn^{2+} and SO_4^{2-} ions in aqueous solution. The anode reaction is the oxidation half-reaction:



The zinc metal, in producing Zn^{2+} ions that go into solution, is giving up electrons, which flow through the wire. For now, we will assume that all cell components are in their standard states, so in this case the solution in the anode compartment will contain 1 M Zn^{2+} . The cathode reaction of this cell is the reduction half-reaction:



The cathode consists of a platinum electrode (used because it is a chemically inert conductor) in contact with 1 M H^+ ions and bathed by hydrogen gas at 1 atm. Such an electrode, called the **standard hydrogen electrode**, is shown in Fig. 17.5(b).

Although we can measure the *total* potential of this cell (0.76 V), there is no way to measure the potentials of the individual electrode processes. Thus, if we want potentials for the half-reactions (half-cells), we must arbitrarily divide the total cell potential. For example, if we assign the reaction



where

$$[\text{H}^+] = 1\text{ M} \quad \text{and} \quad P_{\text{H}_2} = 1\text{ atm}$$

a potential of exactly zero volts, then the reaction



will have a potential of 0.76 V because

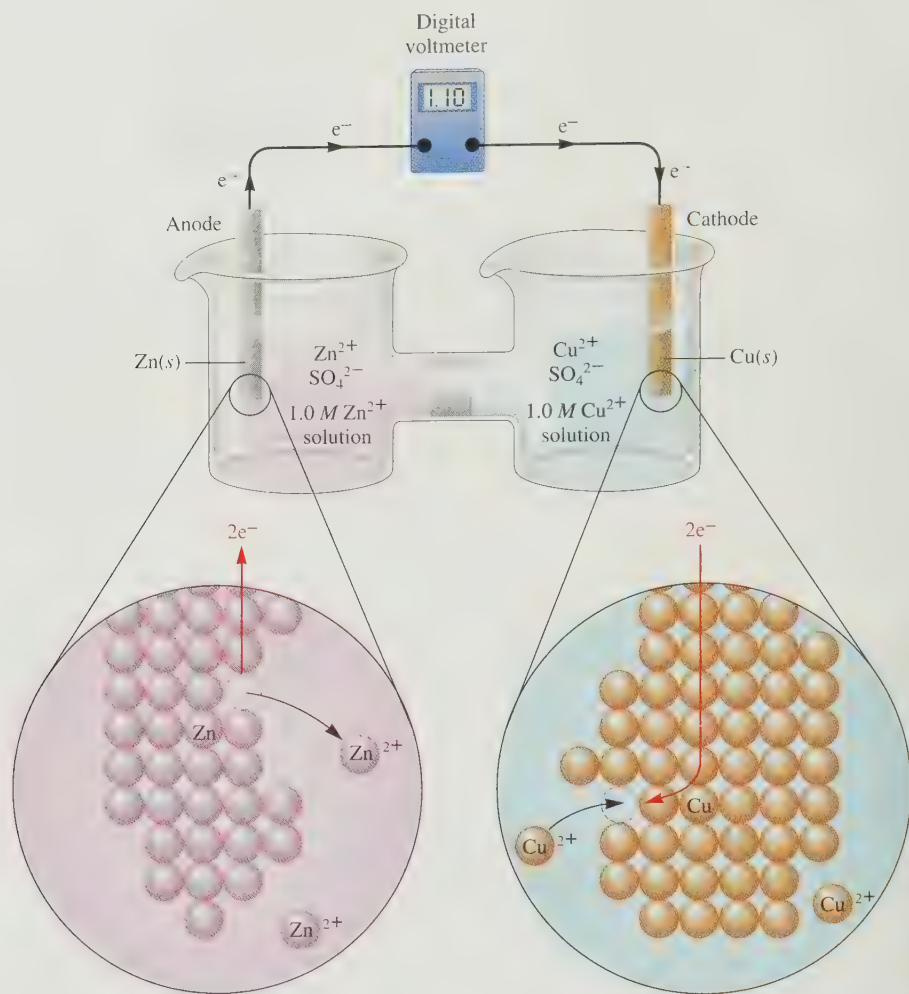
$$\begin{array}{ccccc} \mathcal{E}_{\text{cell}}^\circ & = & \mathcal{E}_{\text{H}^+ \rightarrow \text{H}_2}^\circ & + & \mathcal{E}_{\text{Zn} \rightarrow \text{Zn}^{2+}}^\circ \\ \uparrow & & \uparrow & & \uparrow \\ 0.76\text{ V} & & 0\text{ V} & & 0.76\text{ V} \end{array}$$

where the superscript $^\circ$ indicates that *standard states* are employed. In fact, by setting the standard potential for the half-reaction $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ equal to zero, we can assign values to all other half-reactions.



Visualization: Electrochemical Half-Reactions in a Galvanic Cell

Standard states were discussed in Section 6.4.

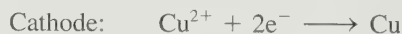
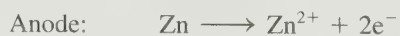
**FIGURE 17.6**

A galvanic cell involving the half-reactions $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$ (anode) and $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$ (cathode), with $\mathcal{E}_{\text{cell}}^{\circ} = 1.10 \text{ V}$.

For example, the measured potential for the cell shown in Fig. 17.6 is 1.10 V. The cell reaction is



which can be divided into the half-reactions



Then

$$\mathcal{E}_{\text{cell}}^{\circ} = \mathcal{E}_{\text{Zn} \rightarrow \text{Zn}^{2+}}^{\circ} + \mathcal{E}_{\text{Cu}^{2+} \rightarrow \text{Cu}}^{\circ}$$

Since $\mathcal{E}_{\text{Zn} \rightarrow \text{Zn}^{2+}}^{\circ}$ was earlier assigned a value of 0.76 V, the value of $\mathcal{E}_{\text{Cu}^{2+} \rightarrow \text{Cu}}^{\circ}$ must be 0.34 V because

$$1.10 \text{ V} = 0.76 \text{ V} + 0.34 \text{ V}$$

The standard hydrogen potential is the reference potential against which all half-reaction potentials are assigned.

The scientific community has universally accepted the half-reaction potentials based on the assignment of zero volts to the process $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ (under standard conditions where ideal behavior is assumed). However, before we can use these

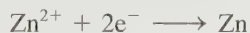
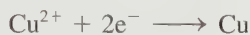
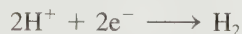
TABLE 17.1 Standard Reduction Potentials at 25°C (298 K) for Many Common Half-Reactions

Half-Reaction	$\mathcal{E}^\circ$ (V)	Half-Reaction	$\mathcal{E}^\circ$ (V)
$\text{F}_2 + 2\text{e}^- \rightarrow 2\text{F}^-$	2.87	$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$	0.40
$\text{Ag}^{2+} + \text{e}^- \rightarrow \text{Ag}^+$	1.99	$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$	0.34
$\text{Co}^{3+} + \text{e}^- \rightarrow \text{Co}^{2+}$	1.82	$\text{Hg}_2\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Hg} + 2\text{Cl}^-$	0.27
$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}$	1.78	$\text{AgCl} + \text{e}^- \rightarrow \text{Ag} + \text{Cl}^-$	0.22
$\text{Ce}^{4+} + \text{e}^- \rightarrow \text{Ce}^{3+}$	1.70	$\text{SO}_4^{2-} + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{SO}_3 + \text{H}_2\text{O}$	0.20
$\text{PbO}_2 + 4\text{H}^+ + \text{SO}_4^{2-} + 2\text{e}^- \rightarrow \text{PbSO}_4 + 2\text{H}_2\text{O}$	1.69	$\text{Cu}^{2+} + \text{e}^- \rightarrow \text{Cu}^+$	0.16
$\text{MnO}_4^- + 4\text{H}^+ + 3\text{e}^- \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$	1.68	$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	0.00
$2\text{e}^- + 2\text{H}^+ + \text{IO}_4^- \rightarrow \text{IO}_3^- + \text{H}_2\text{O}$	1.60	$\text{Fe}^{3+} + 3\text{e}^- \rightarrow \text{Fe}$	-0.036
$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$	1.51	$\text{Pb}^{2+} + 2\text{e}^- \rightarrow \text{Pb}$	-0.13
$\text{Au}^{3+} + 3\text{e}^- \rightarrow \text{Au}$	1.50	$\text{Sn}^{2+} + 2\text{e}^- \rightarrow \text{Sn}$	-0.14
$\text{PbO}_2 + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{Pb}^{2+} + 2\text{H}_2\text{O}$	1.46	$\text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni}$	-0.23
$\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-$	1.36	$\text{PbSO}_4 + 2\text{e}^- \rightarrow \text{Pb} + \text{SO}_4^{2-}$	-0.35
$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	1.33	$\text{Cd}^{2+} + 2\text{e}^- \rightarrow \text{Cd}$	-0.40
$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$	1.23	$\text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe}$	-0.44
$\text{MnO}_2 + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O}$	1.21	$\text{Cr}^{3+} + \text{e}^- \rightarrow \text{Cr}^{2+}$	-0.50
$\text{IO}_3^- + 6\text{H}^+ + 5\text{e}^- \rightarrow \frac{1}{2}\text{I}_2 + 3\text{H}_2\text{O}$	1.20	$\text{Cr}^{3+} + 3\text{e}^- \rightarrow \text{Cr}$	-0.73
$\text{Br}_2 + 2\text{e}^- \rightarrow 2\text{Br}^-$	1.09	$\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$	-0.76
$\text{VO}_2^+ + 2\text{H}^+ + \text{e}^- \rightarrow \text{VO}^{2+} + \text{H}_2\text{O}$	1.00	$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$	-0.83
$\text{AuCl}_4^- + 3\text{e}^- \rightarrow \text{Au} + 4\text{Cl}^-$	0.99	$\text{Mn}^{2+} + 2\text{e}^- \rightarrow \text{Mn}$	-1.18
$\text{NO}_3^- + 4\text{H}^+ + 3\text{e}^- \rightarrow \text{NO} + 2\text{H}_2\text{O}$	0.96	$\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$	-1.66
$\text{ClO}_2 + \text{e}^- \rightarrow \text{ClO}_2^-$	0.954	$\text{H}_2 + 2\text{e}^- \rightarrow 2\text{H}^+$	-2.23
$2\text{Hg}^{2+} + 2\text{e}^- \rightarrow \text{Hg}_2^{2+}$	0.91	$\text{Mg}^{2+} + 2\text{e}^- \rightarrow \text{Mg}$	-2.37
$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$	0.80	$\text{La}^{3+} + 3\text{e}^- \rightarrow \text{La}$	-2.37
$\text{Hg}_2^{2+} + 2\text{e}^- \rightarrow 2\text{Hg}$	0.80	$\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$	-2.71
$\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$	0.77	$\text{Ca}^{2+} + 2\text{e}^- \rightarrow \text{Ca}$	-2.76
$\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2$	0.68	$\text{Ba}^{2+} + 2\text{e}^- \rightarrow \text{Ba}$	-2.90
$\text{MnO}_4^- + \text{e}^- \rightarrow \text{MnO}_4^{2-}$	0.56	$\text{K}^+ + \text{e}^- \rightarrow \text{K}$	-2.92
$\text{I}_2 + 2\text{e}^- \rightarrow 2\text{I}^-$	0.54	$\text{Li}^+ + \text{e}^- \rightarrow \text{Li}$	-3.05
$\text{Cu}^+ + \text{e}^- \rightarrow \text{Cu}$	0.52		

**Video: Galvanic (Voltaic) Cells**

values to calculate cell potentials, we need to understand several essential characteristics of half-cell potentials.

The accepted convention is to give the potentials of half-reactions as *reduction* processes; for example:



All half-reactions are given as reduction processes in standard tables.

The $\mathcal{E}^\circ$ values corresponding to reduction half-reactions with all solutes at 1 M and all gases at 1 atm are called **standard reduction potentials**. Standard reduction potentials for the most common half-reactions are given in Table 17.1 and Appendix 5.5.

Combining two half-reactions to obtain a balanced oxidation–reduction reaction often requires two manipulations:

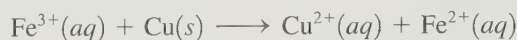
1. One of the reduction half-reactions must be reversed (since redox reactions must involve a substance being oxidized and a substance being reduced), which means that the *sign* of the potential for the reversed half-reaction also must be *reversed*.

When a half-reaction is reversed, the sign of $\mathcal{E}^\circ$ is reversed.

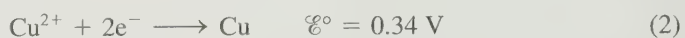
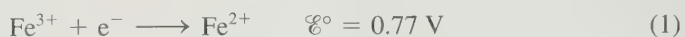
When a half-reaction is multiplied by an integer, $\mathcal{E}^\circ$ remains the same.

2. Since the number of electrons lost must equal the number gained, the half-reactions must be multiplied by integers as necessary to achieve the balanced equation. However, the value of $\mathcal{E}^\circ$ is not changed when a half-reaction is multiplied by an integer. Since a standard reduction potential is an *intensive property* (it does not depend on how many times the reaction occurs), the potential is not multiplied by the integer required to balance the cell reaction.

Consider a galvanic cell based on the redox reaction



The pertinent half-reactions are



To balance the cell reaction and calculate the standard cell potential, reaction (2) must be reversed:

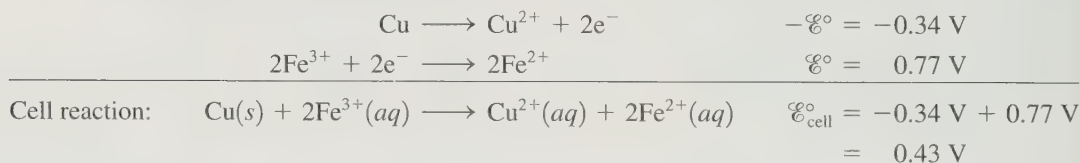


Note the change in sign for the $\mathcal{E}^\circ$ value. Now, since each Cu atom produces two electrons but each Fe^{3+} ion accepts only one electron, reaction (1) must be multiplied by 2:



Note that $\mathcal{E}^\circ$ is not changed in this case.

Now we can obtain the balanced cell reaction by summing the appropriately modified half-reactions:



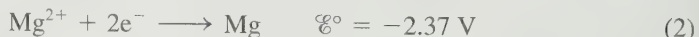
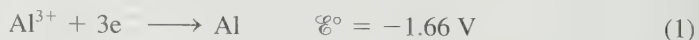
SAMPLE EXERCISE 17.1

Galvanic Cells

- a. Consider a galvanic cell based on the reaction



The half-reactions are

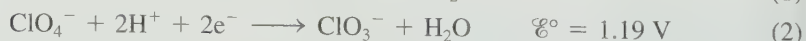
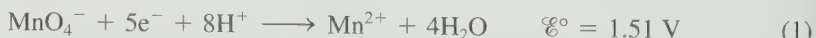


Give the balanced cell reaction and calculate $\mathcal{E}^\circ$ for the cell.

- b. A galvanic cell is based on the reaction



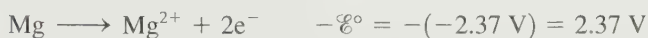
The half-reactions are



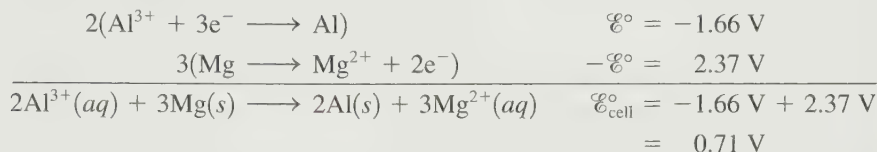
Give the balanced cell reaction and calculate $\mathcal{E}^\circ$ for the cell.

SOLUTION

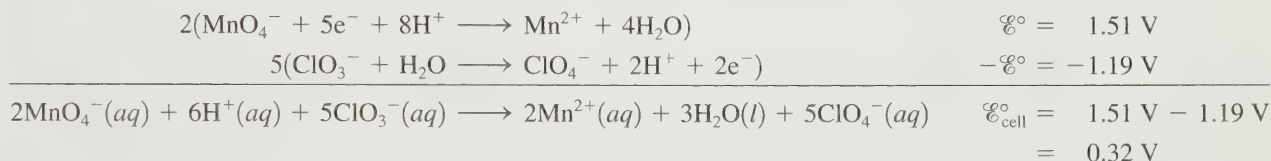
a. The half-reaction involving magnesium must be reversed:



Also, since the two half-reactions involve different numbers of electrons, they must be multiplied by integers as follows:



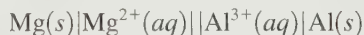
b. Half-reaction (2) must be reversed, and both half-reactions must be multiplied by integers to make the number of electrons equal:



See Exercises 17.27 and 17.28.

Line Notation

We now will introduce a handy line notation used to describe electrochemical cells. In this notation the anode components are listed on the left and the cathode components are listed on the right, separated by double vertical lines (indicating the salt bridge or porous disk). For example, the line notation for the cell described in Sample Exercise 17.1(a) is



In this notation a phase difference (boundary) is indicated by a single vertical line. Thus, in this case, vertical lines occur between the solid Mg metal and the Mg^{2+} in aqueous solution and between solid Al and Al^{3+} in aqueous solution. Also note that the substance constituting the anode is listed at the far left and the substance constituting the cathode is listed at the far right.

For the cell described in Sample Exercise 17.1(b), all the components involved in the oxidation–reduction reaction are ions. Since none of these dissolved ions can serve as an electrode, a nonreacting (inert) conductor must be used. The usual choice is platinum. Thus, for the cell described in Sample Exercise 17.1(b), the line notation is



Complete Description of a Galvanic Cell

Next we want to consider how to describe a galvanic cell fully, given just its half-reactions. This description will include the cell reaction, the cell potential, and the physical setup of the cell. Let's consider a galvanic cell based on the following half-reactions:

A galvanic cell runs spontaneously in the direction that gives a positive value for $\mathcal{E}_{\text{cell}}$.



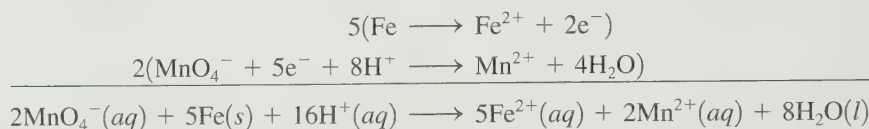
In a working galvanic cell, one of these reactions must run in reverse. Which one?

We can answer this question by considering the sign of the potential of a working cell: *A cell will always run spontaneously in the direction that produces a positive cell potential.* Thus, in the present case, it is clear that the half-reaction involving iron must be reversed, since this choice leads to a positive cell potential:



where $\mathcal{E}_{\text{cell}}^\circ = 0.44 \text{ V} + 1.51 \text{ V} = 1.95 \text{ V}$

The balanced cell reaction is obtained as follows:



Now consider the physical setup of the cell, shown schematically in Fig. 17.7. In the left compartment the active components in their standard states are pure metallic iron (Fe) and 1.0 M Fe^{2+} . The anion present depends on the iron salt used. In this compartment the anion does not participate in the reaction but simply balances the charge. The half-reaction that takes place at this electrode is



which is an oxidation reaction, so this compartment is the anode. The electrode consists of pure iron metal.

In the right compartment the active components in their standard states are 1.0 M MnO_4^- , 1.0 M H^+ , and 1.0 M Mn^{2+} , with appropriate unreacting ions (often called *counterions*) to balance the charge. The half-reaction in this compartment is

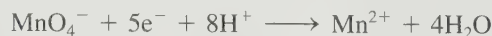


which is a reduction reaction, so this compartment is the cathode. Since neither MnO_4^- nor Mn^{2+} ions can serve as the electrode, a nonreacting conductor such as platinum must be employed.

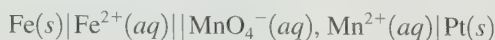
The next step is to determine the direction of electron flow. In the left compartment the half-reaction involves the oxidation of iron:



In the right compartment the half-reaction is the reduction of MnO_4^- :



Thus the electrons flow from Fe to MnO_4^- in this cell, or from the anode to the cathode, as is always the case. The line notation for this cell is



A complete description of a galvanic cell usually includes four items:

- The cell potential (always positive for a galvanic cell) and the balanced cell reaction.

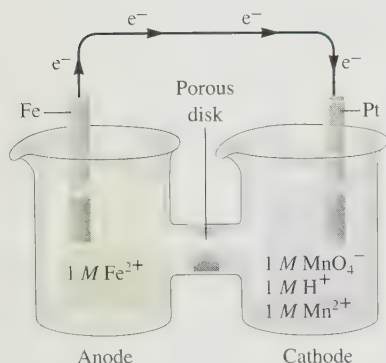
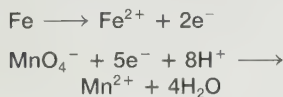


FIGURE 17.7

The schematic of a galvanic cell based on the half-reactions:

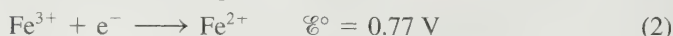
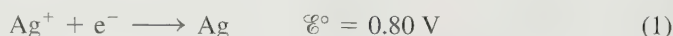


- The direction of electron flow, obtained by inspecting the half-reactions and using the direction that gives a positive $\mathcal{E}_{\text{cell}}$.
- Designation of the anode and cathode.
- The nature of each electrode and the ions present in each compartment. A chemically inert conductor is required if none of the substances participating in the half-reaction is a conducting solid.

SAMPLE EXERCISE 17.2

Description of a Galvanic Cell

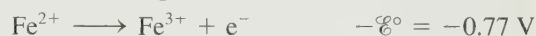
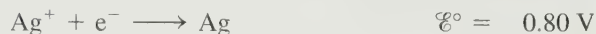
Describe completely the galvanic cell based on the following half-reactions under standard conditions:



SOLUTION

Item 1

Since a positive $\mathcal{E}_{\text{cell}}^\circ$ value is required, reaction (2) must run in reverse:



Item 2

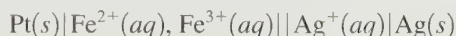
Since Ag^+ receives electrons and Fe^{2+} loses electrons in the cell reaction, the electrons will flow from the compartment containing Fe^{2+} to the compartment containing Ag^+ .

Item 3

Oxidation occurs in the compartment containing Fe^{2+} (electrons flow from Fe^{2+} to Ag^+). Hence this compartment functions as the anode. Reduction occurs in the compartment containing Ag^+ , so this compartment functions as the cathode.

Item 4

The electrode in the Ag/Ag^+ compartment is silver metal, and an inert conductor, such as platinum, must be used in the $\text{Fe}^{2+}/\text{Fe}^{3+}$ compartment. Appropriate counterions are assumed to be present. The diagram for this cell is shown in Fig. 17.8. The line notation for this cell is



See Exercises 17.29 and 17.30.

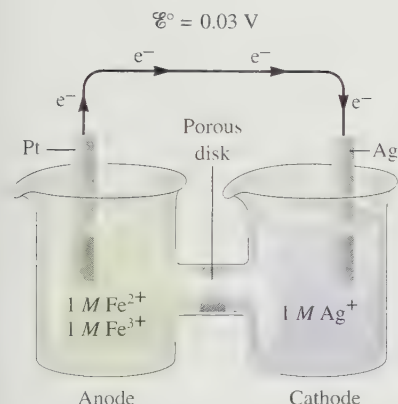
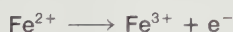


FIGURE 17.8

Schematic diagram for the galvanic cell based on the half-reactions



17.3 Cell Potential, Electrical Work, and Free Energy

So far we have considered electrochemical cells in a very practical fashion without much theoretical background. The next step will be to explore the relationship between thermodynamics and electrochemistry.

The work that can be accomplished when electrons are transferred through a wire depends on the “push” (the thermodynamic driving force) behind the electrons. This driving force (the emf) is defined in terms of a *potential difference* (in volts)



Using a battery-powered drill to insert a screw.

Work is never the maximum possible if any current is flowing.

between two points in the circuit. Recall that a volt represents a joule of work per coulomb of charge transferred:

$$\text{emf} = \text{potential difference (V)} = \frac{\text{work (J)}}{\text{charge (C)}}$$

Thus 1 joule of work is produced or required (depending on the direction) when 1 coulomb of charge is transferred between two points in the circuit that differ by a potential of 1 volt.

In this book, *work is viewed from the point of view of the system*. Thus work flowing out of the system is indicated by a minus sign. When a cell produces a current, the cell potential is positive, and the current can be used to do work—to run a motor, for instance. Thus the cell potential $\mathcal{E}$ and the work w have opposite signs:

$$\mathcal{E} = \frac{-w \leftarrow \text{Work}}{q \leftarrow \text{Charge}}$$

Therefore,

$$-w = q\mathcal{E}$$

From this equation it can be seen that the maximum work in a cell would be obtained at the maximum cell potential:

$$-w_{\text{max}} = q\mathcal{E}_{\text{max}} \quad \text{or} \quad w_{\text{max}} = -q\mathcal{E}_{\text{max}}$$

However, there is a problem. To obtain electrical work, current must flow. When current flows, some energy is inevitably wasted through frictional heating, and the maximum work is not obtained. This reflects the important general principle introduced in Section 16.9: *In any real, spontaneous process some energy is always wasted—the actual work realized is always less than the calculated maximum*. This is a consequence of the fact that the entropy of the universe must increase in any spontaneous process. Recall from Section 16.9 that the only process from which maximum work could be realized is the hypothetical reversible process. For a galvanic cell this would involve an infinitesimally small current flow and thus an infinite amount of time to do the work. Even though we can never achieve the maximum work through the actual discharge of a galvanic cell, we can measure the maximum potential. There is negligible current flow when a cell potential is measured with a potentiometer or an efficient digital voltmeter. No current flow implies no waste of energy, so the potential measured is the maximum.

Although we can never actually realize the maximum work from a cell reaction, the value for it is still useful in evaluating the efficiency of a real process based on the cell reaction. For example, suppose a certain galvanic cell has a maximum potential (at zero current) of 2.50 V. In a particular experiment 1.33 moles of electrons were passed through this cell at an average actual potential of 2.10 V. The actual work done is

$$w = -q\mathcal{E}$$

where $\mathcal{E}$ represents the actual potential difference at which the current flowed (2.10 V or 2.10 J/C) and q is the quantity of charge in coulombs transferred. The charge on 1 mole of electrons is a constant called the **faraday** (abbreviated F), which has the value 96,485 coulombs of charge per mole of electrons. Thus q equals the number of moles of electrons times the charge per mole of electrons:

$$q = nF = 1.33 \text{ mol e}^- \times 96,485 \text{ C/mol e}^-$$



Michael Faraday lecturing at the Royal Institution before Prince Albert and others (1855). The faraday was named in honor of Michael Faraday (1791–1867), an Englishman who may have been the greatest experimental scientist of the nineteenth century. Among his many achievements were the invention of the electric motor and generator and the development of the principles of electrolysis.

Then, for the preceding experiment, the actual work is

$$\begin{aligned} w &= -q\mathcal{E} = -(1.33 \text{ mol e}^- \times 96,485 \text{ C/mol e}^-) \times (2.10 \text{ J/C}) \\ &= -2.69 \times 10^5 \text{ J} \end{aligned}$$

For the maximum possible work, the calculation is similar, except that the maximum potential is used:

$$\begin{aligned} w_{\max} &= -q\mathcal{E} \\ &= -\left(1.33 \text{ mol e}^- \times 96,485 \frac{\text{C}}{\text{mol e}^-}\right) \left(2.50 \frac{\text{J}}{\text{C}}\right) \\ &= -3.21 \times 10^5 \text{ J} \end{aligned}$$

Thus, in its actual operation, the efficiency of this cell is

$$\frac{w}{w_{\max}} \times 100\% = \frac{-2.69 \times 10^5 \text{ J}}{-3.21 \times 10^5 \text{ J}} \times 100\% = 83.8\%$$

Next we want to relate the potential of a galvanic cell to free energy. In Section 16.9 we saw that for a process carried out at constant temperature and pressure, the change in free energy equals the maximum useful work obtainable from that process:

$$w_{\max} = \Delta G$$

For a galvanic cell,

$$w_{\max} = -q\mathcal{E}_{\max} = \Delta G$$

Since

$$q = nF$$

we have

$$\Delta G = -q\mathcal{E}_{\max} = -nF\mathcal{E}_{\max}$$

From now on the subscript on $\mathcal{E}_{\max}$ will be deleted, with the understanding that any potential given in this book is the maximum potential. Thus

$$\Delta G = -nF\mathcal{E}$$

For standard conditions,

$$\Delta G^\circ = -nF\mathcal{E}^\circ$$

This equation states that *the maximum cell potential is directly related to the free energy difference between the reactants and the products in the cell*. This relationship is important because it provides an experimental means to obtain ΔG for a reaction. It also confirms that a galvanic cell will run in the direction that gives a positive value for $\mathcal{E}_{\text{cell}}$; a positive $\mathcal{E}_{\text{cell}}$ value corresponds to a negative ΔG value, which is the condition for spontaneity.

SAMPLE EXERCISE 17.3

Calculating ΔG° for a Cell Reaction

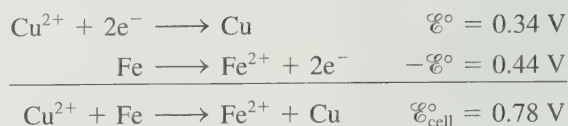
Using the data in Table 17.1, calculate ΔG° for the reaction



Is this reaction spontaneous?

SOLUTION

The half-reactions are



We can calculate ΔG° from the equation

$$\Delta G^\circ = -nF\mathcal{E}^\circ$$

Since two electrons are transferred per atom in the reaction, 2 moles of electrons are required per mole of reactants and products. Thus $n = 2 \text{ mol e}^-$, $F = 96,485 \text{ C/mol e}^-$, and $\mathcal{E}^\circ = 0.78 \text{ V} = 0.78 \text{ J/C}$. Therefore,

$$\begin{aligned}
 \Delta G^\circ &= -(2 \text{ mol e}^-) \left(96,485 \frac{\text{C}}{\text{mol e}^-} \right) \left(0.78 \frac{\text{J}}{\text{C}} \right) \\
 &= -1.5 \times 10^5 \text{ J}
 \end{aligned}$$

The process is spontaneous, as indicated by both the negative sign of ΔG° and the positive sign of $\mathcal{E}_{\text{cell}}^\circ$.

This reaction is used industrially to deposit copper metal from solutions resulting from the dissolving of copper ores.

See Exercises 17.37 and 17.38.

SAMPLE EXERCISE 17.4

Predicting Spontaneity

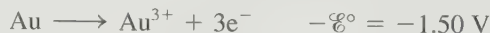
Using the data from Table 17.1, predict whether 1 M HNO_3 will dissolve gold metal to form a 1 M Au^{3+} solution.

SOLUTION

The half-reaction for HNO_3 acting as an oxidizing agent is



The reaction for the oxidation of solid gold to Au^{3+} ions is



The sum of these half-reactions gives the required reaction:



and

$$\mathcal{E}_{\text{cell}}^\circ = 0.96 \text{ V} - 1.50 \text{ V} = -0.54 \text{ V}$$

Since the $\mathcal{E}^\circ$ value is negative, the process will *not* occur under standard conditions. That is, gold will not dissolve in 1 M HNO_3 to give 1 M Au^{3+} . In fact, a mixture (1:3 by volume) of concentrated nitric and hydrochloric acids, called *aqua regia*, is required to dissolve gold.

See Exercises 17.45 and 17.46.



A gold ring does not dissolve in nitric acid.

17.4 Dependence of Cell Potential on Concentration

So far we have described cells under standard conditions. In this section we consider the dependence of the cell potential on concentration. Under standard conditions (all concentrations 1 *M*), the cell with the reaction



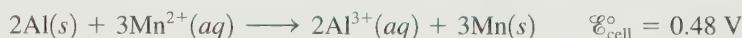
has a potential of 1.36 V. What will the cell potential be if $[\text{Ce}^{4+}]$ is greater than 1.0 *M*? This question can be answered qualitatively in terms of Le Châtelier's principle. An increase in the concentration of Ce^{4+} will favor the forward reaction and thus increase the driving force on the electrons. The cell potential will increase. On the other hand, an increase in the concentration of a product (Cu^{2+} or Ce^{3+}) will oppose the forward reaction, thus decreasing the cell potential.

These ideas are illustrated in Sample Exercise 17.5.

SAMPLE EXERCISE 17.5

The Effects of Concentration on $\mathcal{E}$

For the cell reaction



predict whether $\mathcal{E}_{\text{cell}}$ is larger or smaller than $\mathcal{E}_{\text{cell}}^{\circ}$ for the following cases.

- $[\text{Al}^{3+}] = 2.0 \text{ M}$, $[\text{Mn}^{2+}] = 1.0 \text{ M}$
- $[\text{Al}^{3+}] = 1.0 \text{ M}$, $[\text{Mn}^{2+}] = 3.0 \text{ M}$

SOLUTION

- A product concentration has been raised above 1.0 *M*. This will oppose the cell reaction and will cause $\mathcal{E}_{\text{cell}}$ to be less than $\mathcal{E}_{\text{cell}}^{\circ}$ ($\mathcal{E}_{\text{cell}} < 0.48 \text{ V}$).
- A reactant concentration has been increased above 1.0 *M*, and $\mathcal{E}_{\text{cell}}$ will be greater than $\mathcal{E}_{\text{cell}}^{\circ}$ ($\mathcal{E}_{\text{cell}} > 0.48 \text{ V}$).

See Exercise 17.51.

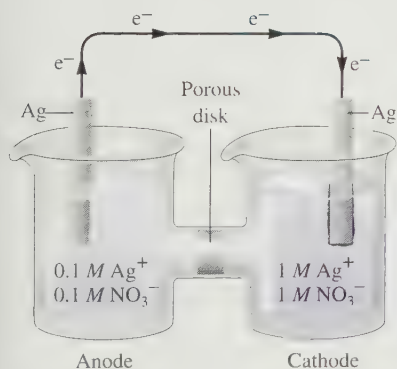


FIGURE 17.9

A concentration cell that contains a silver electrode and aqueous silver nitrate in both compartments. Because the right compartment contains 1 *M* Ag^+ and the left compartment contains 0.1 *M* Ag^+ , there will be a driving force to transfer electrons from left to right. Silver will be deposited on the right electrode, thus lowering the concentration of Ag^+ in the right compartment. In the left compartment the silver electrode dissolves (producing Ag^+ ions) to raise the concentration of Ag^+ in solution.

Concentration Cells

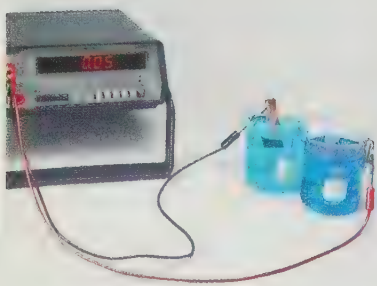
Because cell potentials depend on concentration, we can construct galvanic cells where both compartments contain the same components but at different concentrations. For example, in the cell in Fig. 17.9, both compartments contain aqueous AgNO_3 , but with different molarities. Let's consider the potential of this cell and the direction of electron flow. The half-reaction relevant to both compartments of this cell is



If the cell had 1 *M* Ag^+ in both compartments,

$$\mathcal{E}_{\text{cell}}^{\circ} = 0.80 \text{ V} - 0.80 \text{ V} = 0 \text{ V}$$

However, in the cell described here, the concentrations of Ag^+ in the two compartments are 1 *M* and 0.1 *M*. Because the concentrations of Ag^+ are



A concentration cell with 1.0 M Cu^{2+} on the right and 0.010 M Cu^{2+} on the left.

SAMPLE EXERCISE 17.6

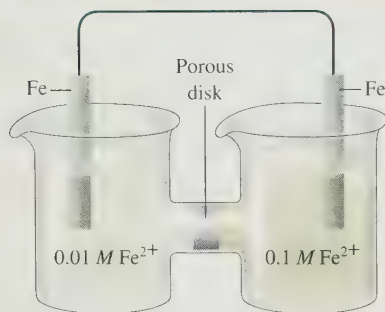


FIGURE 17.10

A concentration cell containing iron electrodes and different concentrations of Fe^{2+} ion in the two compartments.

unequal, the half-cell potentials will not be identical, and the cell will exhibit a positive voltage. In which direction will the electrons flow in this cell? The best way to think about this question is to recognize that nature will try to equalize the concentrations of Ag^+ in the two compartments. This can be done by transferring electrons from the compartment containing 0.1 M Ag^+ to the one containing 1 M Ag^+ (left to right in Fig. 17.9). This electron transfer will produce more Ag^+ in the left compartment and consume Ag^+ (to form Ag) in the right compartment.

A cell in which both compartments have the same components but at different concentrations is called a **concentration cell**. The difference in concentration is the only factor that produces a cell potential in this case, and the voltages are typically small.

Concentration Cells

Determine the direction of electron flow and designate the anode and cathode for the cell represented in Fig. 17.10.

SOLUTION

The concentrations of Fe^{2+} ion in the two compartments can (eventually) be equalized by transferring electrons from the left compartment to the right. This will cause Fe^{2+} to be formed in the left compartment, and iron metal will be deposited (by reducing Fe^{2+} ions to Fe) on the right electrode. Since electron flow is from left to right, oxidation occurs in the left compartment (the anode) and reduction occurs in the right (the cathode).

See Exercise 17.52.

The Nernst Equation

The dependence of the cell potential on concentration results directly from the dependence of free energy on concentration. Recall from Chapter 16 that the equation

$$\Delta G = \Delta G^\circ + RT \ln(Q)$$

where Q is the reaction quotient, was used to calculate the effect of concentration on ΔG . Since $\Delta G = -nF\mathcal{E}$ and $\Delta G^\circ = -nF\mathcal{E}^\circ$, the equation becomes

$$-nF\mathcal{E} = -nF\mathcal{E}^\circ + RT \ln(Q)$$

Dividing each side of the equation by $-nF$ gives

$$\mathcal{E} = \mathcal{E}^\circ - \frac{RT}{nF} \ln(Q) \quad (17.1)$$

Equation (17.1), which gives the relationship between the cell potential and the concentrations of the cell components, is commonly called the **Nernst equation**, after the German chemist Walther Hermann Nernst (1864–1941).

The Nernst equation is often given in a form that is valid at 25°C:

$$\mathcal{E} = \mathcal{E}^\circ - \frac{0.0591}{n} \log(Q)$$

Nernst was one of the pioneers in the development of electrochemical theory and is generally given credit for first stating the third law of thermodynamics. He won the Nobel Prize in chemistry in 1920.

Using this relationship, we can calculate the potential of a cell in which some or all of the components are not in their standard states.

For example, $\mathcal{E}_{\text{cell}}^{\circ}$ is 0.48 V for the galvanic cell based on the reaction



Consider a cell in which

$$[\text{Mn}^{2+}] = 0.50\text{ M} \quad \text{and} \quad [\text{Al}^{3+}] = 1.50\text{ M}$$

The cell potential at 25°C for these concentrations can be calculated using the Nernst equation:

$$\mathcal{E}_{\text{cell}} = \mathcal{E}_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log(Q)$$

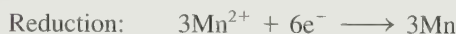
We know that

$$\mathcal{E}_{\text{cell}}^{\circ} = 0.48\text{ V}$$

and

$$Q = \frac{[\text{Al}^{3+}]^2}{[\text{Mn}^{2+}]^3} = \frac{(1.50)^2}{(0.50)^3} = 18$$

Since the half-reactions are



we know that

$$n = 6$$

$$\begin{aligned} \text{Thus} \quad \mathcal{E}_{\text{cell}} &= 0.48 - \frac{0.0591}{6} \log(18) \\ &= 0.48 - \frac{0.0591}{6} (1.26) = 0.48 - 0.01 = 0.47\text{ V} \end{aligned}$$

Note that the cell voltage decreases slightly because of the nonstandard concentrations. This change is consistent with the predictions of Le Châtelier's principle (see Sample Exercise 17.5). In this case, since the reactant concentration is lower than 1.0 M and the product concentration is higher than 1.0 M, $\mathcal{E}_{\text{cell}}$ is less than $\mathcal{E}_{\text{cell}}^{\circ}$.

The potential calculated from the Nernst equation is the maximum potential before any current flow has occurred. As the cell discharges and current flows from anode to cathode, the concentrations will change, and as a result, $\mathcal{E}_{\text{cell}}$ will change. In fact, *the cell will spontaneously discharge until it reaches equilibrium*, at which point

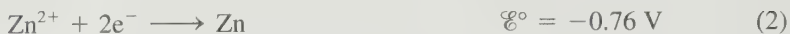
$$Q = K \text{ (the equilibrium constant)} \quad \text{and} \quad \mathcal{E}_{\text{cell}} = 0$$

A “dead” battery is one in which the cell reaction has reached equilibrium, and there is no longer any chemical driving force to push electrons through the wire. In other words, *at equilibrium, the components in the two cell compartments have the same free energy*, and $\Delta G = 0$ for the cell reaction at the equilibrium concentrations. The cell no longer has the ability to do work.

SAMPLE EXERCISE 17.7

The Nernst Equation

Describe the cell based on the following half-reactions:



where

$$T = 25^\circ\text{C}$$

$$[\text{VO}_2^+] = 2.0 \text{ M}$$

$$[\text{H}^+] = 0.50 \text{ M}$$

$$[\text{VO}^{2+}] = 1.0 \times 10^{-2} \text{ M}$$

$$[\text{Zn}^{2+}] = 1.0 \times 10^{-1} \text{ M}$$

SOLUTION

The balanced cell reaction is obtained by reversing reaction (2) and multiplying reaction (1) by 2:



Since the cell contains components at concentrations other than 1 M, we must use the Nernst equation, where $n = 2$ (since two electrons are transferred), to calculate the cell potential. At 25°C we can use the equation

$$\begin{aligned} \mathcal{E} &= \mathcal{E}_{\text{cell}}^\circ - \frac{0.0591}{n} \log(Q) \\ &= 1.76 - \frac{0.0591}{2} \log\left(\frac{[\text{Zn}^{2+}][\text{VO}^{2+}]^2}{[\text{VO}_2^+]^2[\text{H}^+]^4}\right) \\ &= 1.76 - \frac{0.0591}{2} \log\left(\frac{(1.0 \times 10^{-1})(1.0 \times 10^{-2})^2}{(2.0)^2(0.50)^4}\right) \\ &= 1.76 - \frac{0.0591}{2} \log(4 \times 10^{-5}) = 1.76 + 0.13 = 1.89 \text{ V} \end{aligned}$$

The cell diagram is given in Fig. 17.11.

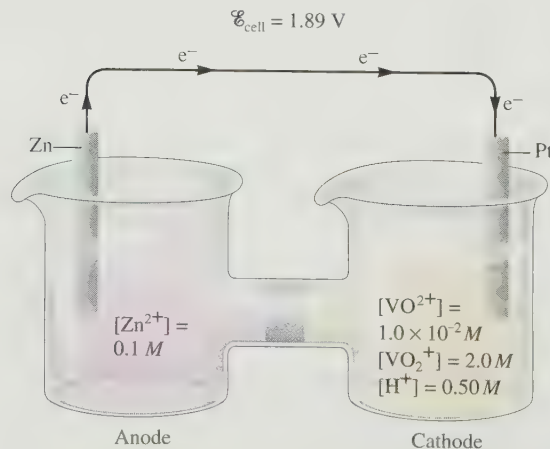


FIGURE 17.11
Schematic diagram of the cell described in Sample Exercise 17.7.

FIGURE 17.12

A glass electrode contains a reference solution of dilute hydrochloric acid in contact with a thin glass membrane in which a silver wire coated with silver chloride has been embedded. When the electrode is dipped into a solution containing H^+ ions, the electrode potential is determined by the difference in $[\text{H}^+]$ between the two solutions.



Ion-Selective Electrodes

Because the cell potential is sensitive to the concentrations of the reactants and products involved in the cell reaction, measured potentials can be used to determine the concentration of an ion. A pH meter (see Fig. 14.9) is a familiar example of an instrument that measures concentration using an observed potential. The pH meter has three main components: a standard electrode of known potential, a special **glass electrode** that changes potential depending on the concentration of H^+ ions in the solution into which it is dipped, and a potentiometer that measures the potential between the electrodes. The potentiometer reading is automatically converted electronically to a direct reading of the pH of the solution being tested.

The glass electrode (see Fig. 17.12) contains a reference solution of dilute hydrochloric acid in contact with a thin glass membrane. The electrical potential of the glass electrode depends on the difference in $[\text{H}^+]$ between the reference solution and the solution into which the electrode is dipped. Thus the electrical potential varies with the pH of the solution being tested.

Electrodes that are sensitive to the concentration of a particular ion are called **ion-selective electrodes**, of which the glass electrode for pH measurement is just one example. Glass electrodes can be made sensitive to such ions as Na^+ , K^+ , or NH_4^+ by changing the composition of the glass. Other ions can be detected if an appropriate crystal replaces the glass membrane. For example, a crystal of lanthanum(III) fluoride (LaF_3) can be used in an electrode to measure $[\text{F}^-]$. Solid silver sulfide (Ag_2S) can be used to measure $[\text{Ag}^+]$ and $[\text{S}^{2-}]$. Some of the ions that can be detected by ion-selective electrodes are listed in Table 17.2.

TABLE 17.2

Some Ions Whose Concentrations Can Be Detected by Ion-Selective Electrodes

Cations	Anions
H^+	Br^-
Cd^{2+}	Cl^-
Ca^{2+}	CN^-
Cu^{2+}	F^-
K^+	NO_3^-
Ag^+	S^{2-}
Na^+	

Calculation of Equilibrium Constants for Redox Reactions

The quantitative relationship between $\mathcal{E}^\circ$ and ΔG° allows calculation of equilibrium constants for redox reactions. For a cell at equilibrium,

$$\mathcal{E}_{\text{cell}} = 0 \quad \text{and} \quad Q = K$$

Applying these conditions to the Nernst equation valid at 25°C,

$$\mathcal{E} = \mathcal{E}^\circ - \frac{0.0591}{n} \log(Q)$$

gives

$$0 = \mathcal{E}^\circ - \frac{0.0591}{n} \log(K)$$

or

$$\log(K) = \frac{n\mathcal{E}^\circ}{0.0591} \quad \text{at } 25^\circ\text{C}$$

SAMPLE EXERCISE 17.8

Equilibrium Constants from Cell Potentials

For the oxidation–reduction reaction



the appropriate half-reactions are

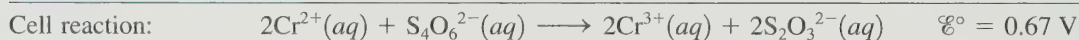
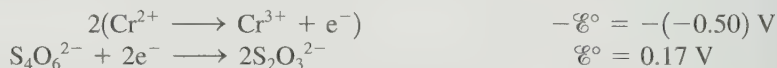


Balance the redox reaction, and calculate $\mathcal{E}^\circ$ and K (at 25°C).

SOLUTION

To obtain the balanced reaction, we must reverse reaction (2), multiply it by 2, and add it to reaction (1):

2 × reaction (2) reversed
Reaction (1)



In this reaction, 2 moles of electrons are transferred for every unit of reaction, that is, for every 2 mol Cr^{2+} reacting with 1 mol $\text{S}_4\text{O}_6^{2-}$ to form 2 mol Cr^{3+} and 2 mol $\text{S}_2\text{O}_3^{2-}$. Thus $n = 2$. Then

$$\log(K) = \frac{n\mathcal{E}^\circ}{0.0591} = \frac{2(0.67)}{0.0591} = 22.6$$

The value of K is found by taking the antilog of 22.6:

$$K = 10^{22.6} = 4 \times 10^{22}$$

This very large equilibrium constant is not unusual for a redox reaction.

See Exercises 17.63 through 17.66.



The blue solution contains Cr^{2+} ions, and the green solution contains Cr^{3+} ions.

17.5 Batteries

A **battery** is a galvanic cell or, more commonly, a group of galvanic cells connected in series, where the potentials of the individual cells add to give the total battery potential. Batteries are a source of direct current and have become an essential source of portable power in our society. In this section we examine the most common types of batteries. Some new batteries currently being developed are described at the end of the chapter.

CHEMICAL IMPACT

Printed Batteries

Soon you may reach for a compact disc in your local record store and, as you touch it, the package will start playing one of the songs on the disc. Or you may stop to look at a product because the package begins to glow as you pass it in the store. These effects could happen soon thanks to the invention of a flexible, superthin battery that can actually be printed onto the package. This battery was developed by Power Paper, Ltd., a company founded by Baruch Levanon and several colleagues.

The battery developed by Power Paper consists of five layers of zinc (anode) and manganese dioxide (cathode) and is only 0.5 millimeter thick. The battery can be printed onto paper with a regular printing press and appears to present no environmental hazards.

The new battery has been licensed by International Paper Company, which intends to use it to bring light, sound, and other special effects to packaging to entice potential customers. You might see talking, singing, or glowing packages on the shelves within a year or two.

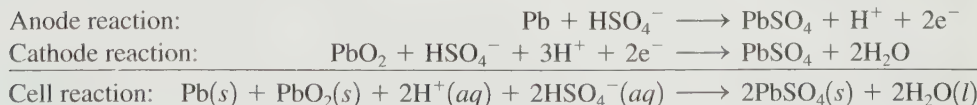


A CD case with an ultrathin battery that can be “printed” on packages like ink.

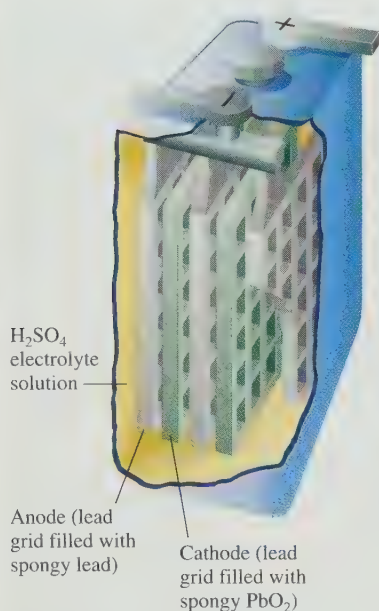
Lead Storage Battery

Since about 1915 when self-starters were first used in automobiles, the **lead storage battery** has been a major factor in making the automobile a practical means of transportation. This type of battery can function for several years under temperature extremes from -30°F to 120°F and under incessant punishment from rough roads.

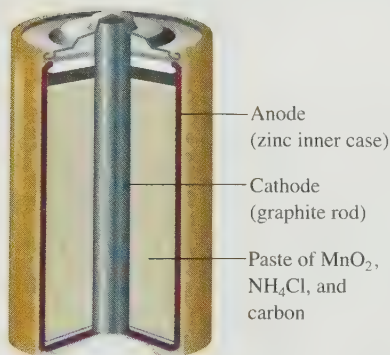
In this battery, lead serves as the anode, and lead coated with lead dioxide serves as the cathode. Both electrodes dip into an electrolyte solution of sulfuric acid. The electrode reactions are



The typical automobile lead storage battery has six cells connected in series. Each cell contains multiple electrodes in the form of grids (Fig. 17.13) and produces approximately 2 V, to give a total battery potential of about 12 V. Note from the cell reaction that sulfuric acid is consumed as the battery discharges. This lowers the density of the electrolyte solution from its initial value of about 1.28 g/cm^3 in the fully charged battery. As a result, the condition of the battery can be monitored by measuring the density of the sulfuric acid solution. The solid lead sulfate formed in

**FIGURE 17.13**

One of the six cells in a 12-V lead storage battery. The anode consists of a lead grid filled with spongy lead, and the cathode is a lead grid filled with lead dioxide. The cell also contains 38% (by mass) sulfuric acid.

**FIGURE 17.14**

A common dry cell battery.

the cell reaction during discharge adheres to the grid surfaces of the electrodes. The battery is recharged by forcing current through it in the opposite direction to reverse the cell reaction. A car's battery is continuously charged by an alternator driven by the automobile engine.

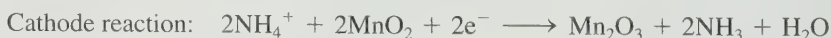
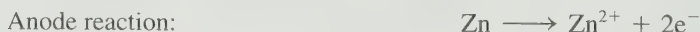
An automobile with a dead battery can be "jump-started" by connecting its battery to the battery in a running automobile. This process can be dangerous, however, because the resulting flow of current causes electrolysis of water in the dead battery, producing hydrogen and oxygen gases (see Section 17.7 for details). Disconnecting the jumper cables after the disabled car starts causes an arc that can ignite the gaseous mixture. If this happens, the battery may explode, ejecting corrosive sulfuric acid. This problem can be avoided by connecting the ground jumper cable to a part of the engine remote from the battery. Any arc produced when this cable is disconnected will then be harmless.

Traditional types of storage batteries require periodic "topping off" because the water in the electrolyte solution is depleted by the electrolysis that accompanies the charging process. Recent types of batteries have electrodes made of an alloy of calcium and lead that inhibits the electrolysis of water. These batteries can be sealed, since they require no addition of water.

It is rather amazing that in the 85 years in which lead storage batteries have been used, no better system has been found. Although a lead storage battery does provide excellent service, it has a useful lifetime of 3 to 5 years in an automobile. While it might seem that the battery could undergo an indefinite number of discharge/charge cycles, physical damage from road shock and chemical side-reactions eventually cause it to fail.

Other Batteries

The calculators, electronic games, digital watches, and portable CD players that are so familiar to us are all powered by small, efficient batteries. The common **dry cell battery** was invented more than 100 years ago by George Leclanché (1839–1882), a French chemist. In its *acid version*, the dry cell battery contains a zinc inner case that acts as the anode and a carbon rod in contact with a moist paste of solid MnO_2 , solid NH_4Cl , and carbon that acts as the cathode (Fig. 17.14). The half-reactions are complex but can be approximated as follows:



This cell produces a potential of about 1.5 V.

In the *alkaline version* of the dry cell battery, the solid NH_4Cl is replaced with KOH or NaOH . In this case the half-reactions can be approximated as follows:



The alkaline dry cell lasts longer mainly because the zinc anode corrodes less rapidly under basic conditions than under acidic conditions.

Other types of useful batteries include the *silver cell*, which has a Zn anode and a cathode that employs Ag_2O as the oxidizing agent in a basic environment. *Mercury cells*, often used in calculators, have a Zn anode and a cathode involving HgO as the oxidizing agent in a basic medium (see Fig. 17.15).

An especially important type of battery is the *nickel-cadmium battery*, in which the electrode reactions are

Now there is an emerging technology, called *thermophotovoltaics* (TPV), that uses a heat source instead of the sun for energy. These devices can operate at night or on an overcast day without a battery. Although TPV devices could use many different sources of heat, the examples currently under development use a propane burner. To produce an electric current, the radiant heat from the burner is used to excite a “radiator,” a device that emits infrared (IR) radiation when heated. The emitted IR radiation then falls on a “converter,” which is a semiconductor that contains p–n junctions. The IR radiation excites electrons from valence bands to conduction bands in the semiconductor so that the electrons can flow as a current. A schematic of a TPV generator is illustrated in the diagram.

Although TPV technology is still in its infancy, it has many possible uses. The utilization of industrial waste

Another promising application of TPV technology is for cars with hybrid energy sources. For example, an experimental electric car built at Western Washington University uses a 10-kw TPV generator to supplement the batteries that serve as the main power source.

Projections indicate that TPV devices could account for \$500 million in sales by 2005, mainly by substituting TPV generators for small diesel-powered generators used on boats and by the military in the field. It appears that this technology has a hot future.

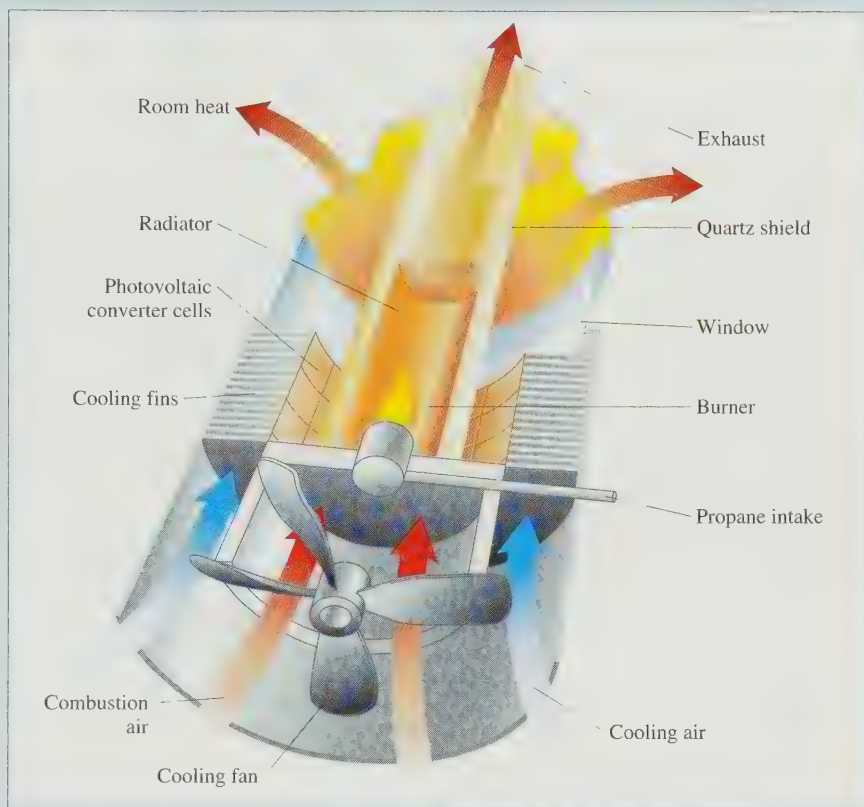


Diagram of a TPV generator.



Batteries for electronic watches are, by necessity, very tiny.

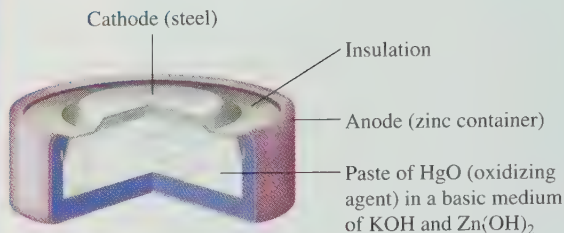
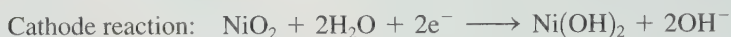


FIGURE 17.15
A mercury battery of the type used in calculators.



As in the lead storage battery, the products adhere to the electrodes. Therefore, a nickel–cadmium battery can be recharged an indefinite number of times.

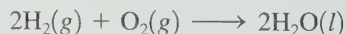
Fuel Cells

A **fuel cell** is a galvanic cell for which the reactants are continuously supplied. To illustrate the principles of fuel cells, let's consider the exothermic redox reaction of methane with oxygen:

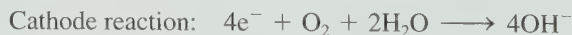
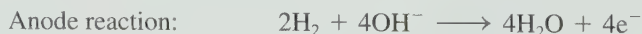


Usually the energy from this reaction is released as heat to warm homes and to run machines. However, in a fuel cell designed to use this reaction, the energy is used to produce an electric current: The electrons flow from the reducing agent (CH_4) to the oxidizing agent (O_2) through a conductor.

The U.S. space program has supported extensive research to develop fuel cells. The space shuttle uses a fuel cell based on the reaction of hydrogen and oxygen to form water:



A schematic of a fuel cell that employs this reaction is shown in Fig. 17.16. The half-reactions are



A cell of this type weighing about 500 pounds has been designed for space vehicles, but this fuel cell is not practical enough for general use as a source of portable power. However, current research on portable electrochemical power is now proceeding at a rapid pace. In fact, cars powered by fuel cells are now being tested on the streets.

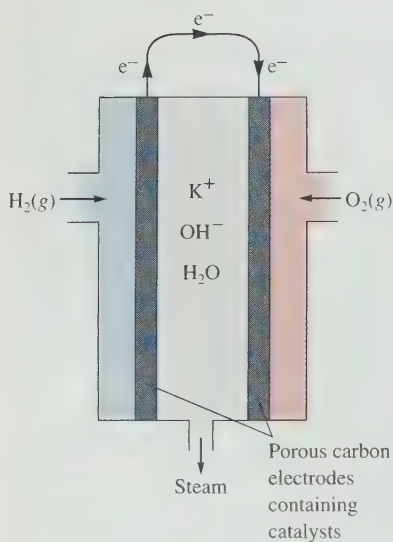


FIGURE 17.16
Schematic of the hydrogen–oxygen fuel cell.

CHEMICAL IMPACT

Fuel Cells for Cars

Your next car may be powered by a fuel cell. Until recently only affordable to NASA, fuel cells are now ready to become practical power plants in cars. Many car companies are testing vehicles that should be commercially available by 2004 or 2005. All of these vehicles are powered by hydrogen/oxygen fuel cells (see Fig. 17.16).

One of the most common types of fuel cells for automobiles uses a proton-exchange membrane (PEM). When H_2 releases electrons at the anode, H^+ ions form and then travel through the membrane to the cathode, where they combine with O_2 and electrons to form water. This cell generates about 0.7 V of power. To achieve the desired power level, several cells are stacked in series. Fuel cells of this type have appeared in several prototype vehicles, such as Nissan's Xterra FCV, Ford's Focus FCV, and DaimlerChrysler's Mercedes Benz NECAR 5 (see photo).

The main question yet to be answered deals with whether the fuel cells in these cars will be fueled by H_2 stored on board or by H_2 made from gasoline or methanol as it is needed. The latter systems include an onboard reformer that uses catalysts to produce H_2 from other fuels. The on-board storage of hydrogen could take place in a tank at high pressure (approximately 5000 psi) or it could utilize a metal-hydride-based solid. Energy Conversion Devices



A gathering of several cars powered by fuel cells (Los Angeles Memorial Coliseum).

(ECD) of Troy, Michigan, is developing a storage system based on a magnesium alloy that absorbs H_2 to form a magnesium hydride. The H_2 gas can be released from this solid by heating it to $300^\circ C$. According to ECD, the alloy can be fully charged with H_2 in about 5 minutes, achieving a hydrogen density of 103 g/L. This density compares to 71 g/L for liquid hydrogen and 31 g/L for gaseous hydrogen at 5000 psi. ECD claims its storage system furnishes enough H_2 to power a fuel-cell car for 300 miles of driving.

Clearly, fuel-cell-powered cars are on the near horizon.

Fuel cells are also finding use as permanent power sources. For example, a power plant built in New York City contains stacks of hydrogen-oxygen fuel cells, which can be rapidly put on-line in response to fluctuating power demands. The hydrogen gas is obtained by decomposing the methane in natural gas. A plant of this type also has been constructed in Tokyo.

In addition, new fuel cells are under development that can use fuels such as methane and diesel directly without having to produce hydrogen first.

17.6 Corrosion

Corrosion can be viewed as the process of returning metals to their natural state—the ores from which they were originally obtained. Corrosion involves oxidation of the metal. Since corroded metal often loses its structural integrity and attractiveness,

Some metals, such as copper, gold, silver, and platinum, are relatively difficult to oxidize. These are often called *noble metals*.

this spontaneous process has great economic impact. Approximately one-fifth of the iron and steel produced annually is used to replace rusted metal.

Metals corrode because they oxidize easily. Table 17.1 shows that, with the exception of gold, those metals commonly used for structural and decorative purposes all have standard reduction potentials less positive than that of oxygen gas. When any of these half-reactions is reversed (to show oxidation of the metal) and combined with the reduction half-reaction for oxygen, the result is a positive $\mathcal{E}^\circ$ value. Thus the oxidation of most metals by oxygen is spontaneous (although we cannot tell from the potential how fast it will occur).

In view of the large difference in reduction potentials between oxygen and most metals, it is surprising that the problem of corrosion does not completely prevent the use of metals in air. However, most metals develop a thin oxide coating, which tends to protect their internal atoms against further oxidation. The metal that best demonstrates this phenomenon is aluminum. With a reduction potential of -1.7 V, aluminum should be easily oxidized by O_2 . According to the apparent thermodynamics of the reaction, an aluminum airplane could dissolve in a rainstorm. The fact that this very active metal can be used as a structural material is due to the formation of a thin, adherent layer of aluminum oxide (Al_2O_3), more properly represented as $Al_2(OH)_6$, which greatly inhibits further corrosion. The potential of the “passive,” oxide-coated aluminum is -0.6 V, a value that causes it to behave much like a noble metal.

Iron also can form a protective oxide coating. This coating is not an infallible shield against corrosion, however; when steel is exposed to oxygen in moist air, the oxide that forms tends to scale off and expose new metal surfaces to corrosion.

The corrosion products of noble metals such as copper and silver are complex and affect the use of these metals as decorative materials. Under normal atmospheric conditions, copper forms an external layer of greenish copper carbonate called *patina*. *Silver tarnish* is silver sulfide (Ag_2S), which in thin layers gives the silver surface a richer appearance. Gold, with a positive standard reduction potential of 1.50 V, significantly larger than that for oxygen (1.23 V), shows no appreciable corrosion in air.

Corrosion of Iron

Since steel is the main structural material for bridges, buildings, and automobiles, controlling its corrosion is extremely important. To do this, we must understand the corrosion mechanism. Instead of being a direct oxidation process as we might expect, the corrosion of iron is an electrochemical reaction, as shown in Fig. 17.17.

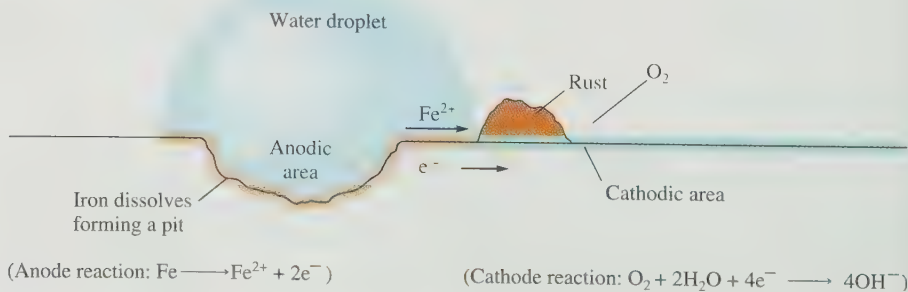


FIGURE 17.17
The electrochemical corrosion of iron.

CHEMICAL IMPACT

Paint That Stops Rust—Completely

Traditionally, paint has provided the most economical method for protecting steel against corrosion. However, as people who live in the Midwest know well, paint cannot prevent a car from rusting indefinitely. Eventually, flaws develop in the paint that allow the ravages of rusting to take place.

This situation may soon change. Chemists at Glidden Research Center in Ohio have developed a paint called Rustmaster Pro that worked so well to prevent rusting in its initial tests that the scientists did not believe their results. Steel coated with the new paint showed no signs of rusting after an astonishing 10,000 hours of exposure in a salt spray chamber at 38°C.

Rustmaster is a water-based polymer formulation that prevents corrosion in two different ways. First, the polymer layer that cures in air forms a barrier impenetrable to both oxygen and water vapor. Second, the chemicals in the coating react with the steel surface to produce an interlayer between the metal and the polymer coating. This interlayer is a complex mineral called *pyroaurite* that contains cations of

the form $[M_{1-x}Z_x(OH)_2]^{x+}$, where M is a 2+ ion (Mg^{2+} , Fe^{2+} , Zn^{2+} , Co^{2+} , or Ni^{2+}), Z is a 3+ ion (Al^{3+} , Fe^{3+} , Mn^{3+} , Co^{3+} , or Ni^{3+}), and x is a number between 0 and 1. The anions in pyroaurite are typically CO_3^{2-} , Cl^- , and/or SO_4^{2-} .

This pyroaurite interlayer is the real secret of the paint's effectiveness. Because the corrosion of steel has an electrochemical mechanism, motion of ions must be possible between the cathodic and anodic areas on the surface of the steel for rusting to occur. However, the pyroaurite interlayer grows into the neighboring polymer layer, thus preventing this crucial movement of ions. In effect, this layer prevents corrosion in the same way that removing the salt bridge prevents current from flowing in a galvanic cell.

In addition to having an extraordinary corrosion-fighting ability, Rustmaster yields an unusually small quantity of volatile solvents as it dries. A typical paint can produce from 1 to 5 kg of volatiles per gallon; Rustmaster produces only 0.05 kg. This paint may signal a new era in corrosion prevention.

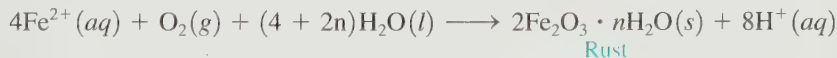
Steel has a nonuniform surface because the chemical composition is not completely homogeneous. Also, physical strains leave stress points in the metal. These nonuniformities cause areas where the iron is more easily oxidized (*anodic regions*) than it is at others (*cathodic regions*). In the anodic regions each iron atom gives up two electrons to form the Fe^{2+} ion:



The electrons that are released flow through the steel, as they do through the wire of a galvanic cell, to a cathodic region, where they react with oxygen:



The Fe^{2+} ions formed in the anodic regions travel to the cathodic regions through the moisture on the surface of the steel, just as ions travel through a salt bridge in a galvanic cell. In the cathodic regions Fe^{2+} ions react with oxygen to form rust, which is hydrated iron(III) oxide of variable composition:



Because of the migration of ions and electrons, rust often forms at sites that are remote from those where the iron dissolved to form pits in the steel. The degree of hydration of the iron oxide affects the color of the rust, which may vary from black to yellow to the familiar reddish brown.

The electrochemical nature of the rusting of iron explains the importance of moisture in the corrosion process. Moisture must be present to act as a kind of salt bridge between anodic and cathodic regions. Steel does not rust in dry air, a fact that explains why cars last much longer in the arid Southwest than in the relatively

humid Midwest. Salt also accelerates rusting, a fact all too easily recognized by car owners in the colder parts of the United States, where salt is used on roads to melt snow and ice. The severity of rusting is greatly increased because the dissolved salt on the moist steel surface increases the conductivity of the aqueous solution formed there and thus accelerates the electrochemical corrosion process. Chloride ions also form very stable complex ions with Fe^{3+} , and this factor tends to encourage the dissolving of the iron, again accelerating the corrosion.

Prevention of Corrosion

Prevention of corrosion is an important way of conserving our natural resources of energy and metals. The primary means of protection is the application of a coating, most commonly paint or metal plating, to protect the metal from oxygen and moisture. Chromium and tin are often used to plate steel (see Section 17.8) because they oxidize to form a durable, effective oxide coating. Zinc, also used to coat steel in a process called **galvanizing**, forms a mixed oxide-carbonate coating. Since zinc is a more active metal than iron, as the potentials for the oxidation half-reactions show:



any oxidation that occurs dissolves zinc rather than iron. Recall that the reaction with the most positive standard potential has the greatest thermodynamic tendency to occur. Thus zinc acts as a “sacrificial” coating on steel.

Alloying is also used to prevent corrosion. *Stainless steel* contains chromium and nickel, both of which form oxide coatings that change steel’s reduction potential to one characteristic of the noble metals. In addition, a new technology is now being developed to create surface alloys. That is, instead of forming a metal alloy such as stainless steel, which has the same composition throughout, a cheaper carbon steel is treated by ion bombardment to produce a thin layer of stainless steel or other desirable alloy on the surface. In this process, a “plasma” or “ion gas” of the alloying ions is formed at high temperatures and is then directed onto the surface of the metal.

Cathodic protection is a method most often employed to protect steel in buried fuel tanks and pipelines. An active metal, such as magnesium, is connected by a wire to the pipeline or tank to be protected (Fig. 17.18). Because the magnesium is a better reducing agent than iron, electrons are furnished by the magnesium rather than by the iron, keeping the iron from being oxidized. As oxidation occurs, the magnesium anode dissolves, and so it must be replaced periodically. Ships’ hulls

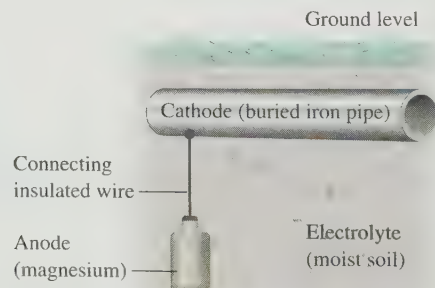


FIGURE 17.18
Cathodic protection of an underground pipe.

are protected in a similar way by attaching bars of titanium metal to the steel hull (Fig. 17.18). In salt water the titanium acts as the anode and is oxidized instead of the steel hull (the cathode).

17.7 Electrolysis

An electrolytic cell uses electrical energy to produce a chemical change that would otherwise not occur spontaneously.

A galvanic cell produces current when an oxidation–reduction reaction proceeds spontaneously. A similar apparatus, an **electrolytic cell**, uses electrical energy to produce chemical change. The process of **electrolysis** involves *forcing a current through a cell to produce a chemical change for which the cell potential is negative*; that is, electrical work causes an otherwise nonspontaneous chemical reaction to occur. Electrolysis has great practical importance; for example, charging a battery, producing aluminum metal, and chrome plating an object are all done electrolytically.

To illustrate the difference between a galvanic cell and an electrolytic cell, consider the cell shown in Fig. 17.19(a) as it runs spontaneously to produce 1.10 V. In this *galvanic* cell the reaction at the anode is



whereas at the cathode the reaction is

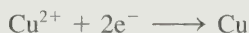


Figure 17.19(b) shows an external power source forcing electrons through the cell in the *opposite* direction to that in (a). This requires an external potential greater than 1.10 V, which must be applied in opposition to the natural cell potential. This device is an *electrolytic cell*. Notice that since electron flow is opposite in the two cases, the anode and cathode are reversed between (a) and (b). Also, ion flow through the salt bridge is opposite in the two cells.

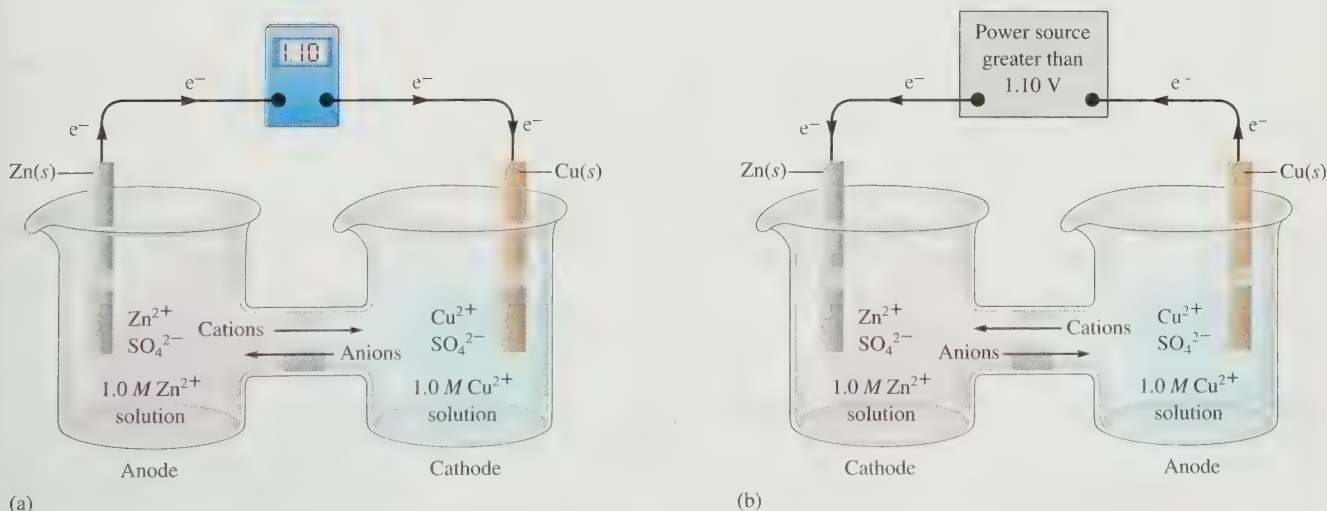


FIGURE 17.19

(a) A standard galvanic cell based on the spontaneous reaction

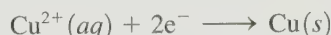


(b) A standard electrolytic cell. A power source forces the opposite reaction



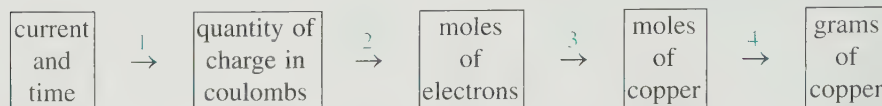
$$1 \text{ A} = 1 \text{ C/s}$$

Now we will consider the stoichiometry of electrolytic processes, that is, *how much chemical change occurs with the flow of a given current for a specified time*. Suppose we wish to determine the mass of copper that is plated out when a current of 10.0 amps (an **ampere** [amp], abbreviated A, is *1 coulomb of charge per second*) is passed for 30.0 minutes through a solution containing Cu^{2+} . *Plating* means depositing the neutral metal on the electrode by reducing the metal ions in solution. In this case each Cu^{2+} ion requires two electrons to become an atom of copper metal:



This reduction process will occur at the cathode of the electrolytic cell.

To solve this stoichiometry problem, we need the following steps:



- ➡ **1** Since an amp is a coulomb of charge per second, we multiply the current by the time in seconds to obtain the total coulombs of charge passed into the Cu^{2+} solution at the cathode:

$$\begin{aligned} \text{Coulombs of charge} &= \text{amps} \times \text{seconds} = \frac{\text{C}}{\text{s}} \times \text{s} \\ &= 10.0 \frac{\text{C}}{\text{s}} \times 30.0 \text{ min} \times 60.0 \frac{\text{s}}{\text{min}} \\ &= 1.80 \times 10^4 \text{ C} \end{aligned}$$

- ➡ **2** Since 1 mole of electrons carries a charge of 1 faraday, or 96,485 coulombs, we can calculate the number of moles of electrons required to carry 1.80×10^4 coulombs of charge:

$$1.80 \times 10^4 \text{ C} \times \frac{1 \text{ mol e}^{-}}{96,485 \text{ C}} = 1.87 \times 10^{-1} \text{ mol e}^{-}$$

This means that 0.187 mole of electrons flowed into the Cu^{2+} solution.

- ➡ **3** Each Cu^{2+} ion requires two electrons to become a copper atom. Thus each mole of electrons produces $\frac{1}{2}$ mole of copper metal:

$$1.87 \times 10^{-1} \text{ mol e}^{-} \times \frac{1 \text{ mol Cu}}{2 \text{ mol e}^{-}} = 9.35 \times 10^{-2} \text{ mol Cu}$$

- ➡ **4** We now know the moles of copper metal plated onto the cathode, and we can calculate the mass of copper formed:

$$9.35 \times 10^{-2} \text{ mol Cu} \times \frac{63.546 \text{ g}}{\text{mol Cu}} = 5.94 \text{ g Cu}$$

SAMPLE EXERCISE 17.9

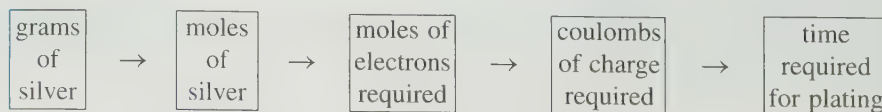
Sample Exercise 17.9 describes only the half-cell of interest. There also must be an anode at which oxidation is occurring.

Electroplating

How long must a current of 5.00 A be applied to a solution of Ag^{+} to produce 10.5 g silver metal?

SOLUTION

In this case, we must use the steps given earlier in reverse:



$$10.5 \text{ g Ag} \times \frac{1 \text{ mol Ag}}{107.868 \text{ g Ag}} = 9.73 \times 10^{-2} \text{ mol Ag}$$

Each Ag^+ ion requires one electron to become a silver atom:



Thus $9.73 \times 10^{-2} \text{ mol}$ of electrons is required, and we can calculate the quantity of charge carried by these electrons:

$$9.73 \times 10^{-2} \text{ mol e}^- \times \frac{96,485 \text{ C}}{\text{mol e}^-} = 9.39 \times 10^3 \text{ C}$$

The 5.00 A (5.00 C/s) of current must produce $9.39 \times 10^3 \text{ C}$ of charge. Thus

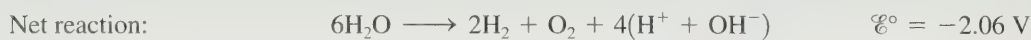
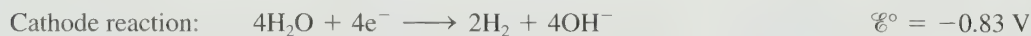
$$\left(5.00 \frac{\text{C}}{\text{s}}\right) \times (\text{time, in s}) = 9.39 \times 10^3 \text{ C}$$

$$\text{Time} = \frac{9.39 \times 10^3}{5.00} \text{ s} = 1.88 \times 10^3 \text{ s} = 31.3 \text{ min}$$

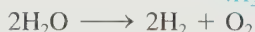
See Exercises 17.73 through 17.76.

Electrolysis of Water

We have seen that hydrogen and oxygen combine spontaneously to form water and that the accompanying decrease in free energy can be used to run a fuel cell to produce electricity. The reverse process, which is of course nonspontaneous, can be forced by electrolysis:



or



Visualization: Electrolysis of Water



FIGURE 17.20
The electrolysis of water produces hydrogen gas at the cathode (on the right) and oxygen gas at the anode (on the left).

Note that these potentials assume an anode chamber with 1 M H^+ and a cathode chamber with 1 M OH^- . In pure water, where $[\text{H}^+] = [\text{OH}^-] = 10^{-7} \text{ M}$, the potential for the overall process is -1.23 V .

In practice, however, if platinum electrodes connected to a 6-V battery are dipped into pure water, no reaction is observed because pure water contains so few ions that only a negligible current can flow. However, addition of even a small amount of a soluble salt causes an immediate evolution of bubbles of hydrogen and oxygen, as illustrated in Fig. 17.20.

Electrolysis of Mixtures of Ions

Suppose a solution in an electrolytic cell contains the ions Cu^{2+} , Ag^+ , and Zn^{2+} . If the voltage is initially very low and is gradually turned up, in which order will the metals be plated out onto the cathode? This question can be answered by looking at the standard reduction potentials of these ions:



CHEMICAL IMPACT

The Chemistry of Sunken Treasure

When the galleon *Atocha* was destroyed on a reef by a hurricane in 1622, it was bound for Spain carrying approximately 47 tons of copper, gold, and silver from the New World. The bulk of the treasure was silver bars and coins packed in wooden chests. When treasure hunter Mel Fisher salvaged the silver in 1985, corrosion and marine growth had transformed the shiny metal into something that looked like coral. Restoring the silver to its original condition required an understanding of the chemical changes that had occurred in 350 years of being submerged in the ocean. Much of this chemistry we have already considered at various places in this text.

As the wooden chests containing the silver decayed, the oxygen supply was depleted, favoring the growth of certain bacteria that use the sulfate ion rather than oxygen as an oxidizing agent to generate energy. As these bacteria consume sulfate ions, they release hydrogen sulfide gas that reacts with silver to form black silver sulfide:

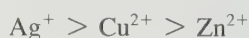


Thus, over the years, the surface of the silver became covered with a tightly adhering layer of corrosion, which fortunately protected the silver underneath and thus prevented total conversion of the silver to silver sulfide.



Silver coins and tankards salvaged from the wreck of the *Atocha*.

Remember that the more *positive* the $\mathcal{E}^\circ$ value, the more the reaction has a tendency to proceed in the direction indicated. Of the three reactions listed, the reduction of Ag^+ occurs most easily, and the order of oxidizing ability is



This means that silver will plate out first as the potential is increased, followed by copper, and finally zinc.

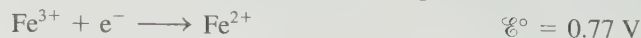
SAMPLE EXERCISE 17.10

Relative Oxidizing Abilities

An acidic solution contains the ions Ce^{4+} , VO_2^+ , and Fe^{3+} . Using the $\mathcal{E}^\circ$ values listed in Table 17.1, give the order of oxidizing ability of these species and predict which one will be reduced at the cathode of an electrolytic cell at the lowest voltage.

SOLUTION

The half-reactions and $\mathcal{E}^\circ$ values are



Another change that took place as the wood decomposed was the formation of carbon dioxide. This shifted the equilibrium that is present in the ocean,



to the right, producing higher concentrations of HCO_3^- . In turn, the HCO_3^- reacted with Ca^{2+} ions present in the seawater to form calcium carbonate:

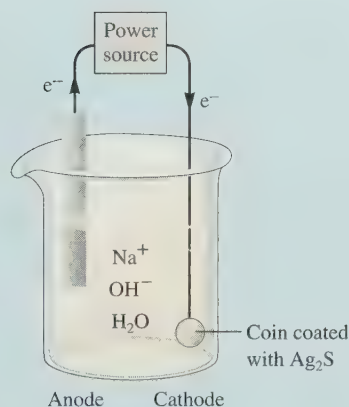


Calcium carbonate is the main component of limestone. Thus, over time, the corroded silver coins and bars became encased in limestone.

Both the limestone formation and the corrosion had to be dealt with. Since CaCO_3 contains the basic anion CO_3^{2-} , acid dissolves limestone:



Soaking the mass of coins in a buffered acidic bath for several hours allowed the individual pieces to be separated, and the black Ag_2S on the surfaces was revealed. An abrasive could not be used to remove this corrosion; it would have destroyed the details of the engraving—a very valuable feature of the coins to a historian or a collector—and it would have washed away some of the silver. Instead, the corrosion reaction was reversed through electrolytic reduction. The coins were connected to the cathode of an electrolytic cell in a dilute sodium hydroxide solution as represented in the figure.



As electrons flow, the Ag^+ ions in the silver sulfide are reduced to silver metal:



As a by-product, bubbles of hydrogen gas from the reduction of water form on the surface of the coins:



The agitation caused by the bubbles loosens the flakes of metal sulfide and helps clean the coins.

These procedures have made it possible to restore the treasure to very nearly its condition when the *Atocha* sailed many years ago.

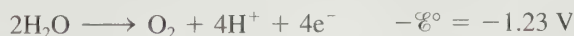
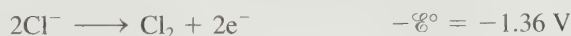
The order of oxidizing ability is therefore



The Ce^{4+} ion will be reduced at the lowest voltage in an electrolytic cell.

See Exercise 17.85.

The principle described in this section is very useful, but it must be applied with some caution. For example, in the electrolysis of an aqueous solution of sodium chloride, we should be able to use $\mathcal{E}^\circ$ values to predict the products. Of the major species in the solution (Na^+ , Cl^- , and H_2O), only Cl^- and H_2O can be readily oxidized. The half-reactions (written as oxidation processes) are



Since water has the more positive potential, we would expect to see O_2 produced at the anode because it is easier (thermodynamically) to oxidize H_2O than Cl^- . Actually, this does not happen. As the voltage is increased in the cell, the Cl^- ion is the first to be oxidized. A much higher potential than expected is required to oxidize

water. The voltage required in excess of the expected value (called the *overvoltage*) is much greater for the production of O_2 than for Cl_2 , which explains why chlorine is produced first.

The causes of overvoltage are very complex. Basically, the phenomenon is caused by difficulties in transferring electrons from the species in the solution to the atoms on the electrode across the electrode–solution interface. Because of this situation, $\mathcal{E}^\circ$ values must be used cautiously in predicting the actual order of oxidation or reduction of species in an electrolytic cell.

17.8 Commercial Electrolytic Processes

The chemistry of metals is characterized by their ability to donate electrons to form ions. Because metals are typically such good reducing agents, most are found in nature in *ores*, mixtures of ionic compounds often containing oxide, sulfide, and silicate anions. The noble metals, such as gold, silver, and platinum, are more difficult to oxidize and are often found as pure metals.

Production of Aluminum

Aluminum is one of the most abundant elements on earth, ranking third behind oxygen and silicon. Since aluminum is a very active metal, it is found in nature as its oxide in an ore called *bauxite* (named after Les Baux, France, where it was discovered in 1821). Production of aluminum metal from its ore proved to be more difficult than production of most other metals. In 1782 Lavoisier recognized aluminum to be a metal “whose affinity for oxygen is so strong that it cannot be overcome by any known reducing agent.” As a result, pure aluminum metal remained unknown. Finally, in 1854 a process was found for producing metallic aluminum using sodium, but aluminum remained a very expensive rarity. In fact, it is said that Napoleon III served his most honored guests with aluminum forks and spoons, while the others had to settle for gold and silver utensils.

The breakthrough came in 1886 when two men, Charles M. Hall in the United States and Paul Heroult in France, almost simultaneously discovered a practical electrolytic process for producing aluminum (see Fig. 17.21). The key factor in the *Hall–Heroult process* is the use of molten cryolite (Na_3AlF_6) as the solvent for the aluminum oxide.

Electrolysis is possible only if ions can move to the electrodes. A common method for producing ion mobility is dissolving the substance to be electrolyzed in water. This is not possible in the case of aluminum because water is more easily reduced than Al^{3+} , as the following standard reduction potentials show:



Thus aluminum metal cannot be plated out of an aqueous solution of Al^{3+} .

Ion mobility also can be produced by melting the salt. But the melting point of solid Al_2O_3 is much too high ($2050^\circ C$) to allow practical electrolysis of the molten oxide. A mixture of Al_2O_3 and Na_3AlF_6 , however, has a melting point of $1000^\circ C$, and the resulting molten mixture can be used to obtain aluminum metal electrolytically. Because of this discovery by Hall and Heroult, the price of aluminum plunged (see Table 17.3), and its use became economically feasible.



FIGURE 17.21

Charles Martin Hall (1863–1914) was a student at Oberlin College in Ohio when he first became interested in aluminum. One of his professors commented that anyone who could manufacture aluminum cheaply would make a fortune, and Hall decided to give it a try. The 21-year-old Hall worked in a wooden shed near his house with an iron frying pan as a container, a blacksmith's forge as a heat source, and galvanic cells constructed from fruit jars. Using these crude galvanic cells, Hall found that he could produce aluminum by passing a current through a molten Al_2O_3/Na_3AlF_6 mixture. By a strange coincidence, Paul Heroult, a Frenchman who was born and died in the same years as Hall, made the same discovery at about the same time.

TABLE 17.3
The Price of Aluminum over
the Past Century

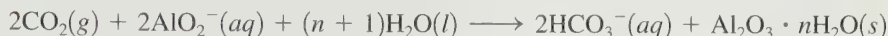
Date	Price of Aluminum (\$/lb)*
1855	100,000
1885	100
1890	2
1895	0.50
1970	0.30
1980	0.80
1990	0.74

*Note the precipitous drop in price after the discovery of the Hall–Heroult process.

Bauxite is not pure aluminum oxide (called *alumina*); it also contains the oxides of iron, silicon, and titanium, and various silicate materials. To obtain the pure hydrated alumina ($\text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$), the crude bauxite is treated with aqueous sodium hydroxide. Being amphoteric, alumina dissolves in the basic solution:



The other metal oxides, which are basic, remain as solids. The solution containing the aluminate ion (AlO_2^-) is separated from the sludge of the other oxides and is acidified with carbon dioxide gas, causing the hydrated alumina to reprecipitate:



The purified alumina is then mixed with cryolite and melted, and the aluminum ion is reduced to aluminum metal in an electrolytic cell of the type shown in Fig. 17.22. Because the electrolyte solution contains a large number of aluminum-containing ions, the chemistry is not completely clear. However, the alumina probably reacts with the cryolite anion as follows:



The electrode reactions are thought to be



The overall cell reaction can be written as



The aluminum produced in this electrolytic process is 99.5% pure. To be useful as a structural material, aluminum is alloyed with metals such as zinc (used for trailer and aircraft construction) and manganese (used for cooking utensils, storage tanks, and highway signs). The production of aluminum consumes about 5% of all the electricity used in the United States.

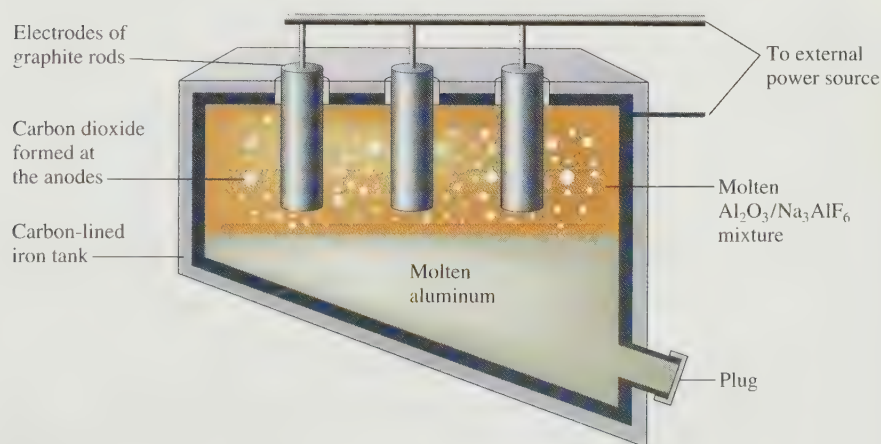


FIGURE 17.22

A schematic diagram of an electrolytic cell for producing aluminum by the Hall–Heroult process. Because molten aluminum is more dense than the mixture of molten cryolite and alumina, it settles to the bottom of the cell and is drawn off periodically. The graphite electrodes are gradually eaten away and must be replaced from time to time. The cell operates at a current flow of up to 250,000 A.

**FIGURE 17.23**

Ultrapure copper sheets that serve as the cathodes are lowered between slabs of impure copper that serve as the anodes into a tank containing an aqueous solution of copper sulfate (CuSO_4). It takes about four weeks for the anodes to dissolve and for the pure copper to be deposited on the cathodes.

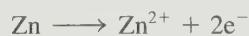
Electrorefining of Metals

Purification of metals is another important application of electrolysis. For example, impure copper from the chemical reduction of copper ore is cast into large slabs that serve as the anodes for electrolytic cells. Aqueous copper sulfate is the electrolyte, and thin sheets of ultrapure copper function as the cathodes (see Fig. 17.23).

The main reaction at the anode is

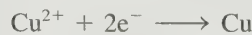


Other metals such as iron and zinc are also oxidized from the impure anode:



Noble metal impurities in the anode are not oxidized at the voltage used; they fall to the bottom of the cell to form a sludge, which is processed to remove the valuable silver, gold, and platinum.

The Cu^{2+} ions from the solution are deposited onto the cathode



producing copper that is 99.95% pure.

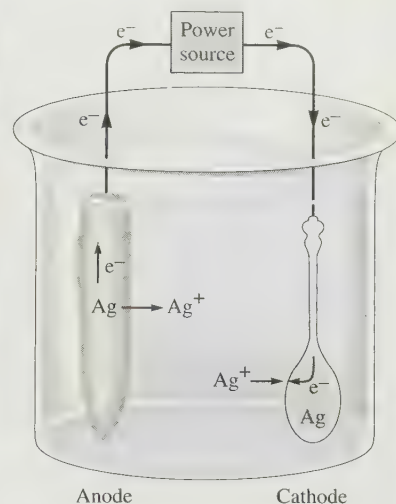
Metal Plating

Metals that readily corrode can often be protected by the application of a thin coating of a metal that resists corrosion. Examples are “tin” cans, which are actually steel cans with a thin coating of tin, and chrome-plated steel bumpers for automobiles.

An object can be plated by making it the cathode in a tank containing ions of the plating metal. The silver plating of a spoon is shown schematically in Fig. 17.24(b). In an actual plating process, the solution also contains ligands that



(a)



(b)

FIGURE 17.24

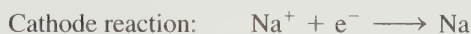
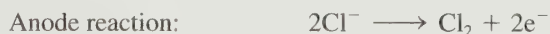
(a) A silver-plated teapot. Silver plating is often used to beautify and protect cutlery and items of table service. (b) Schematic of the electroplating of a spoon. The item to be plated is the cathode, and the anode is a silver bar. Silver is plated out at the cathode: $\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$. Note that a salt bridge is not needed here because Ag^+ ions are involved at both electrodes.

form complexes with the silver ion. By lowering the concentration of Ag^+ in this way, a smooth, even coating of silver is obtained.

Electrolysis of Sodium Chloride

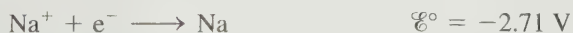
Addition of a nonvolatile solute lowers the melting point of the solvent, molten NaCl in this case.

Sodium metal is mainly produced by the electrolysis of molten sodium chloride. Because solid NaCl has a rather high melting point (800°C), it is usually mixed with solid CaCl_2 to lower the melting point to about 600°C . The mixture is then electrolyzed in a **Downs cell**, as illustrated in Fig. 17.25, where the reactions are



At the temperatures in the Downs cell, the sodium is liquid and is drained off, then cooled, and cast into blocks. Because it is so reactive, sodium must be stored in an inert solvent, such as mineral oil, to prevent its oxidation.

Electrolysis of aqueous sodium chloride (brine) is an important industrial process for the production of chlorine and sodium hydroxide. In fact, this process is the second largest consumer of electricity in the United States, after the production of aluminum. Sodium is not produced in this process under normal circumstances because H_2O is more easily reduced than Na^+ , as the standard reduction potentials show:



Hydrogen, not sodium, is produced at the cathode.

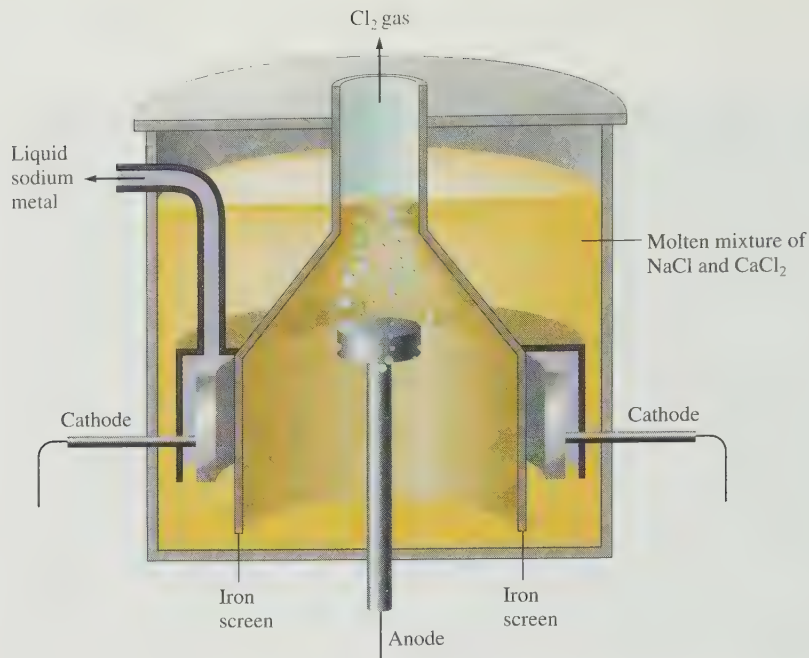
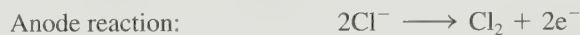


FIGURE 17.25

The Downs cell for the electrolysis of molten sodium chloride. The cell is designed so that the sodium and chlorine produced cannot come into contact with each other to re-form NaCl.

For the reasons we discussed in Section 17.7, chlorine gas is produced at the anode. Thus the electrolysis of brine produces hydrogen and chlorine:



It leaves a solution containing dissolved NaOH and NaCl.

The contamination of the sodium hydroxide by NaCl can be virtually eliminated using a special **mercury cell** for electrolyzing brine (see Fig. 17.26). In this cell, mercury is the conductor at the cathode, and because hydrogen gas has an extremely high overvoltage with a mercury electrode, Na^+ is reduced instead of H_2O .

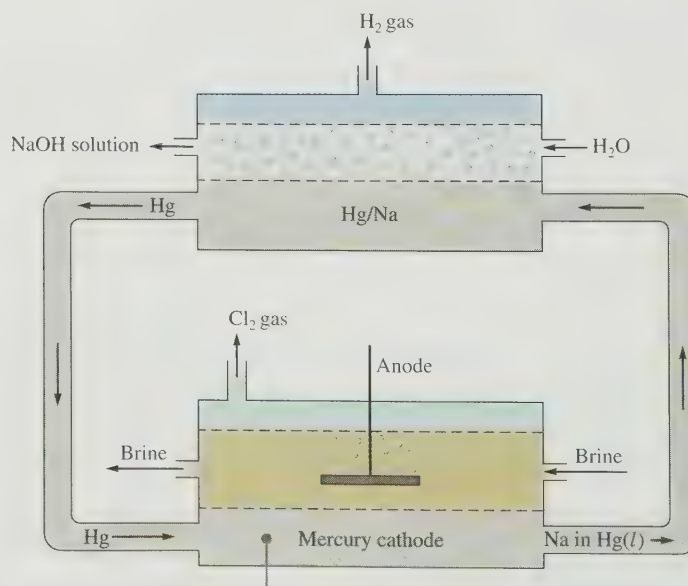


FIGURE 17.26

The mercury cell for production of chlorine and sodium hydroxide. The large overvoltage required to produce hydrogen at a mercury electrode means that Na^+ ions are reduced rather than water. The sodium formed dissolves in the liquid mercury and is pumped to a chamber where it reacts with water.

The resulting sodium metal dissolves in the mercury, forming a liquid alloy, which is then pumped to a chamber where the dissolved sodium reacts with water to produce hydrogen:



Relatively pure solid NaOH can be recovered from the aqueous solution, and the regenerated mercury is then pumped back to the electrolysis cell. This process, called the **chlor-alkali process**, was the main method for producing chlorine and sodium hydroxide in the United States for many years. However, because of the environmental problems associated with the mercury cell, it has been largely displaced in the chlor-alkali industry by other technologies. In the United States, nearly 75 percent of the chlor-alkali production is now carried out in diaphragm cells. In a diaphragm cell the cathode and anode are separated by a diaphragm that allows passage of H_2O molecules, Na^+ ions, and, to a limited extent, Cl^- ions. The diaphragm does not allow OH^- ions to pass through it. Thus the H_2 and OH^- formed at the cathode are kept separate from the Cl_2 formed at the anode. The major disadvantage of this process is that the aqueous effluent pumped from the cathode compartment contains a mixture of sodium hydroxide and unreacted sodium chloride, which must be separated if pure sodium hydroxide is a desired product.

In the past 30 years, a new process has been developed in the chlor-alkali industry that employs a membrane to separate the anode and cathode compartments in brine electrolysis cells. The membrane is superior to a diaphragm because the membrane is impermeable to anions. Only cations can flow through the membrane. Because neither Cl^- nor OH^- ions can pass through the membrane separating the anode and cathode compartments, NaCl contamination of the NaOH formed at the cathode does not occur. Although membrane technology is now just becoming prominent in the United States, it is the dominant method for chlor-alkali production in Japan.

For Review

Summary

Electrochemistry is the study of the interchange of chemical and electrical energy that occurs through oxidation–reduction (redox) reactions, in which electrons are transferred from a reducing agent to an oxidizing agent. Oxidation is the loss of electrons, and reduction is the gain of electrons. It is useful to break a redox reaction into half-reactions, one involving oxidation and one involving reduction.

When a redox reaction occurs in solution, the electrons are transferred directly, and no useful work can be obtained from the chemical energy involved in the reaction. However, if the oxidizing agent is physically separated from the reducing agent so that the electrons must flow through a wire from one to the other, the chemical energy can produce useful work. A galvanic cell is a device in which chemical energy is transformed to electrical energy. The opposite process, where electrical energy is used to produce chemical change, is called electrolysis and is accomplished in an electrolytic cell by forcing current through the cell.

Oxidation occurs at the anode of a cell; reduction occurs at the cathode. The driving force on the electrons is called the cell potential ($\mathcal{E}_{\text{cell}}$). A galvanic cell always runs in the direction that gives a positive value for $\mathcal{E}_{\text{cell}}$. Standard reduction

Key Terms

electrochemistry

Section 17.1

oxidation–reduction (redox) reaction

reducing agent

oxidizing agent

oxidation

reduction

half-reactions

salt bridge

porous disk

galvanic cell

anode

cathode

cell potential (electromotive force)
volt
voltmeter
potentiometer

Section 17.2

standard hydrogen electrode
standard reduction potentials

Section 17.3

faraday

Section 17.4

concentration cell
Nernst equation
glass electrode
ion-selective electrode

Section 17.5

battery
lead storage battery
dry cell battery
fuel cell

Section 17.6

corrosion
galvanizing
cathodic protection

Section 17.7

electrolytic cell
electrolysis
ampere

Section 17.8

Downs cell
mercury cell
chlor-alkali process

potentials are assigned to half-reactions written as reduction processes by arbitrarily assigning a potential of zero volts to the half-reaction $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ under standard conditions.

The unit of electrical potential is the volt (V), defined as a joule of work per coulomb of charge:

$$\mathcal{E} \text{ (V)} = \frac{-\text{work (J)}}{\text{charge (C)}} = \frac{-w}{q}$$

where the sign for work is determined from the point of view of the system (cell). The maximum work can be calculated from the equation

$$-w_{\max} = q\mathcal{E}_{\max}$$

where $\mathcal{E}_{\max}$ represents the cell potential when no current flows. Actual work is always less than the maximum possible work, since energy is wasted through frictional heating when a current flows through a wire.

For a process carried out at constant temperature and pressure, the change in free energy equals the maximum useful work obtainable from that process:

$$\Delta G = w_{\max} = -q\mathcal{E}_{\max} = -nF\mathcal{E}$$

where F (the faraday) is the charge of 1 mole of electrons (96,485 coulombs) and n is the number of moles of electrons transferred in the reaction.

A concentration cell is a galvanic cell in which both compartments have the same components but at different concentrations. The electrons flow in the direction that tends to equalize the concentrations.

The Nernst equation gives the relationship between the cell potential and the concentrations of the cell components:

$$\mathcal{E} = \mathcal{E}^\circ - \frac{RT}{nF} \ln(Q)$$

When the cell is at 25°C, the Nernst equation can be written

$$\mathcal{E} = \mathcal{E}^\circ - \frac{0.0591}{n} \log(Q)$$

When the cell is at equilibrium, $Q = K$ and $\mathcal{E}_{\text{cell}} = 0$. Thus the Nernst equation can be used to calculate the values of equilibrium constants for oxidation–reduction reactions.

A battery is a galvanic cell or group of cells connected in series, which serves as a source of direct current. The lead storage battery has a lead anode, a cathode of lead coated with PbO_2 , and an electrolyte of sulfuric acid. Dry cell batteries do not have liquid electrolytes but have a moist paste of either solid manganese dioxide, carbon, and ammonium chloride (the acid version) or potassium hydroxide or sodium hydroxide (the alkaline version). A case of zinc acts as the anode, and a carbon rod acts as the electrode for the cathode reaction.

Fuel cells are galvanic cells in which the reactants are continuously supplied. For example, a hydrogen–oxygen fuel cell is based on the reaction of hydrogen and oxygen gases to form water.

Corrosion involves the oxidation of metals to form mainly oxides and sulfides. Some metals, such as aluminum, form a thin protective coating of oxide that inhibits further corrosion. The corrosion of iron is an electrochemical process; different parts of the iron surface form anodic and cathodic regions. The Fe^{2+} ions formed

in the anodic regions migrate through the moisture on the iron surface to the cathodic regions, and the electrons flow through the metal to the cathodic regions, where they react with oxygen in the air. Corrosion can be prevented by coating the iron with paint or a layer of a metal such as chromium, tin, or zinc; by alloying; and by cathodic protection.

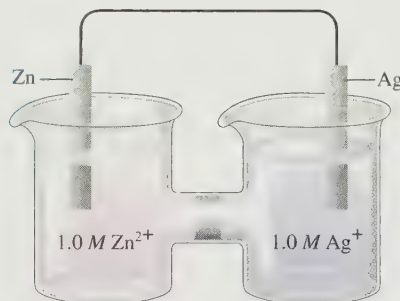
Aluminum is commercially produced by the electrolysis of a molten alumina–cryolite mixture in the Hall–Heroult process. Metals such as copper can be refined electrolytically. The chlor–alkali process is used to manufacture chlorine and sodium hydroxide by electrolysis.

In-Class Discussion Questions

These questions are designed to be considered by groups of students in class. Often these questions work well for introducing a particular topic in class.

1. Sketch a galvanic cell, and explain how it works. Look at Figs. 17.1 and 17.2. Explain what is occurring in each container and why the cell in Fig. 17.2 “works” but the one in Fig. 17.1 does not.
2. In making a specific galvanic cell, explain how one decides on the electrodes and the solutions to use in the cell.
3. You want to “plate out” nickel metal from a nickel nitrate solution onto a piece of metal inserted into the solution. Should you use copper or zinc? Explain.
4. A copper penny can be dissolved in nitric acid but not in hydrochloric acid. Using reduction potentials from the book, show why this is so. What are the products of the reaction? Newer pennies contain a mixture of zinc and copper. What happens to the zinc in the penny when placed in nitric acid? hydrochloric acid? Support your explanations with data from the book, and include balanced equations for all reactions.
5. Sketch a cell that forms iron metal from iron(II) while changing chromium metal to chromium(III). Calculate the voltage, show the electron flow, label the anode and cathode, and balance the overall cell equation.
6. Which of the following is the best reducing agent: F_2 , H_2 , Na , Na^+ , F^- ? Explain. Order as many of these species as possible from the best to the worst oxidizing agent. Why can't you order all of them? From Table 17.1 choose the species that is the best oxidizing agent. Choose the best reducing agent. Explain.
7. You are told that metal A is a better reducing agent than metal B. What, if anything, can be said about A^+ and B^+ ? Explain.
8. Explain the following relationships: ΔG and w , cell potential and w , cell potential and ΔG , cell potential and Q . Using these relationships, explain how you could make a cell in which both electrodes are the same metal and both solutions contain the same compound, but at different concentrations. Why does such a cell run spontaneously?
9. Explain why cell potentials are not multiplied by the coefficients in the balanced redox equation. (Use the relationship between ΔG and cell potential to do this.)

10. What is the difference between $\mathcal{E}$ and $\mathcal{E}^\circ$? When is $\mathcal{E}$ equal to zero? When is $\mathcal{E}^\circ$ equal to zero? (Consider “regular” galvanic cells as well as concentration cells.)
11. Consider the following galvanic cell:



What happens to $\mathcal{E}$ as the concentration of Zn^{2+} is increased? as the concentration of Ag^+ is increased? What happens to $\mathcal{E}^\circ$ in these cases?

12. Look up the reduction potential for Fe^{3+} to Fe^{2+} . Look up the reduction potential for Fe^{2+} to Fe . Finally, look up the reduction potential for Fe^{3+} to Fe . You should notice that adding the reduction potentials for the first two does not give the potential for the third. Why not? Show how you can use the first two potentials to calculate the third potential.

A blue question or exercise number indicates that the answer to that question or exercise appears at the back of this book and a solution appears in the *Solutions Guide*.

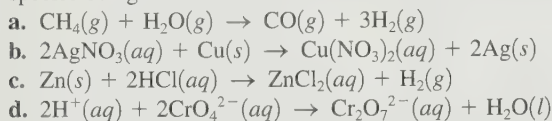
Review of Oxidation–Reduction Reactions

If you have trouble with these exercises, you should review Sections 4.9 and 4.10.

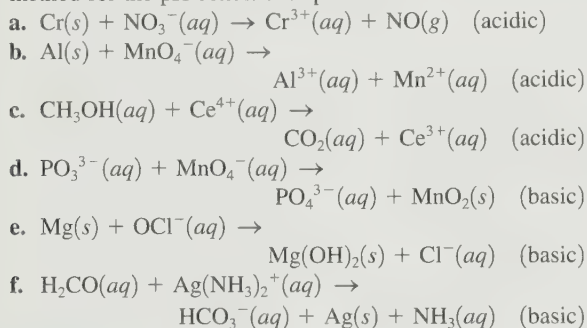
13. Define *oxidation* and *reduction* in terms of both change in oxidation number and electron loss or gain.
14. Assign oxidation numbers to all the atoms in each of the following.

a. HNO_3	e. $MgSO_4$	i. $Na_2C_2O_4$
b. $CuCl_2$	f. Ag	j. CO_2
c. O_2	g. $PbSO_4$	k. $(NH_4)_2Ce(SO_4)_3$
d. H_2O_2	h. PbO_2	l. Cr_2O_3

15. Specify which of the following equations represent oxidation–reduction reactions, and indicate the oxidizing agent, the reducing agent, the species being oxidized, and the species being reduced.



16. Balance each of the following equations by the half-reaction method for the pH conditions specified.



Questions

17. Explain the difference between a galvanic and an electrolytic cell.
 18. Why is it necessary to use a salt bridge or a porous disk in a galvanic cell?
 19. Define the following.
 a. cathode c. oxidation half-reaction
 b. anode d. reduction half-reaction
 20. Describe each of the following.
 a. purification of a metal by electrolysis
 b. cathodic protection
 21. What happens to $\mathcal{E}_{\text{cell}}$ as a battery discharges? Does a battery represent a system at equilibrium? Explain. What is $\mathcal{E}_{\text{cell}}$ when a battery reaches equilibrium?
 22. Why isn't the value of the cell potential multiplied by the same integer used to multiply a half-reaction in balancing the equation for a cell reaction?
 23. How do fuel cells and batteries differ?
 24. Explain how moisture and salt can increase the severity of corrosion. Give three methods by which metals are protected against corrosion.

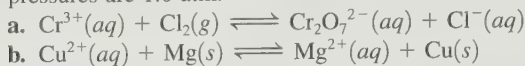
Exercises

In this section similar exercises are paired.

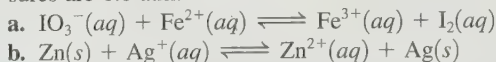
Galvanic Cells, Cell Potentials, Standard Reduction Potentials, and Free Energy

25. Sketch the galvanic cells based on the following overall reactions. Show the direction of electron flow and identify the cathode and anode. Give the overall balanced reaction. As-

sume that all concentrations are 1.0 M and that all partial pressures are 1.0 atm.



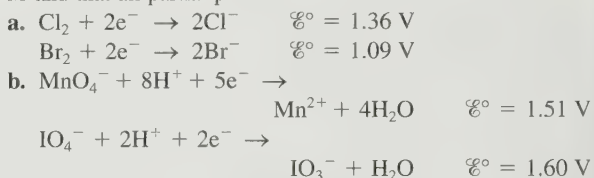
26. Sketch the galvanic cells based on the following overall reactions. Show the direction of electron flow, the direction of ion migration through the salt bridge, and identify the cathode and anode. Give the overall balanced reaction. Assume that all concentrations are 1.0 M and that all partial pressures are 1.0 atm.



27. Calculate $\mathcal{E}^\circ$ values for the galvanic cells in Exercise 25.

28. Calculate $\mathcal{E}^\circ$ values for the galvanic cells in Exercise 26.

29. Sketch the galvanic cells based on the following half-reactions. Show the direction of electron flow, show the direction of ion migration through the salt bridge, and identify the cathode and anode. Give the overall balanced reaction, and determine $\mathcal{E}^\circ$ for the galvanic cells. Assume that all concentrations are 1.0 M and that all partial pressures are 1.0 atm.

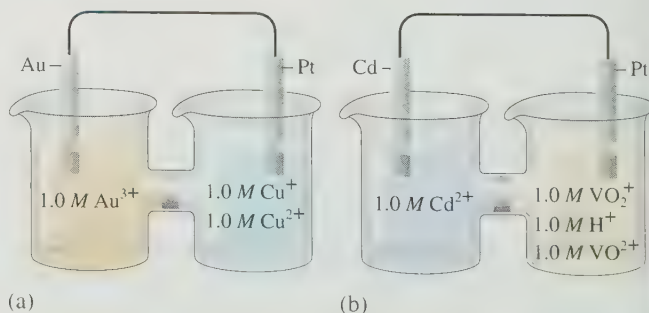


30. Sketch the galvanic cells based on the following half-reactions. Show the direction of electron flow, show the direction of ion migration through the salt bridge, and identify the cathode and anode. Give the overall balanced reaction, and determine $\mathcal{E}^\circ$ for the galvanic cells. Assume that all concentrations are 1.0 M and that all partial pressures are 1.0 atm.
 a. $\text{H}_2\text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow 2\text{H}_2\text{O}$ $\mathcal{E}^\circ = 1.78 \text{ V}$
 $\text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{H}_2\text{O}_2$ $\mathcal{E}^\circ = 0.68 \text{ V}$
 b. $\text{Mn}^{2+} + 2e^- \rightarrow \text{Mn}$ $\mathcal{E}^\circ = -1.18 \text{ V}$
 $\text{Fe}^{3+} + 3e^- \rightarrow \text{Fe}$ $\mathcal{E}^\circ = -0.036 \text{ V}$

31. Give the standard line notation for each cell in Exercises 25 and 29.

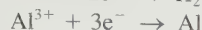
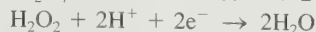
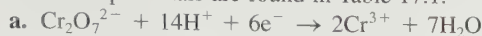
32. Give the standard line notation for each cell in Exercises 26 and 30.

33. Consider the following galvanic cells:

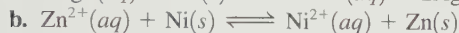


For each galvanic cell, give the balanced cell reaction and determine $\mathcal{E}^\circ$. Standard reduction potentials are found in Table 17.1.

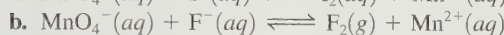
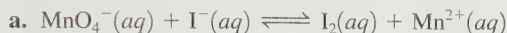
34. Give the balanced cell reaction and determine $\mathcal{E}^\circ$ for the galvanic cells based on the following half-reactions. Standard reduction potentials are found in Table 17.1.



35. Calculate $\mathcal{E}^\circ$ values for the following cells. Which reactions are spontaneous as written (under standard conditions)? Balance the reactions that are not already balanced. Standard reduction potentials are found in Table 17.1.



36. Calculate $\mathcal{E}^\circ$ values for the following cells. Which reactions are spontaneous as written (under standard conditions)? Balance the reactions. Standard reduction potentials are found in Table 17.1.



37. Chlorine dioxide (ClO_2), which is produced by the reaction



has been tested as a disinfectant for municipal water treatment. Using data from Table 17.1, calculate $\mathcal{E}^\circ$ and ΔG° at 25°C for the production of ClO_2 .

38. The amount of manganese in steel is determined by changing it to permanganate ion. The steel is first dissolved in nitric acid, producing Mn^{2+} ions. These ions are then oxidized to the deeply colored MnO_4^- ions by periodate ion (IO_4^-) in acid solution.

a. Complete and balance an equation describing each of the above reactions.

b. Calculate $\mathcal{E}^\circ$ and ΔG° at 25°C for each reaction.

39. Calculate the maximum amount of work that can be obtained from the galvanic cells at standard conditions in Exercise 33.

40. Calculate the maximum amount of work that can be obtained from the galvanic cells at standard conditions in Exercise 34.

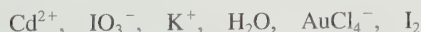
41. Calculate $\mathcal{E}^\circ$ for the reaction



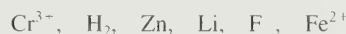
using values of ΔG_f° in Appendix 4.

42. The equation $\Delta G^\circ = -nF\mathcal{E}^\circ$ also can be applied to half-reactions. Use standard reduction potentials to estimate ΔG_f° for $\text{Fe}^{2+}(aq)$ and $\text{Fe}^{3+}(aq)$. (ΔG_f° for $\text{e}^- = 0$.)

43. Using data from Table 17.1, place the following in order of increasing strength as oxidizing agents (all under standard conditions).



44. Using data from Table 17.1, place the following in order of increasing strength as reducing agents (all under standard conditions).



45. Answer the following questions using data from Table 17.1 (all under standard conditions).

a. Is $\text{H}^+(aq)$ capable of oxidizing $\text{Cu}(s)$ to $\text{Cu}^{2+}(aq)$?

b. Is $\text{Fe}^{3+}(aq)$ capable of oxidizing $\text{I}^-(aq)$?

c. Is $\text{H}_2(g)$ capable of reducing $\text{Ag}^+(aq)$?

d. Is $\text{Fe}^{2+}(aq)$ capable of reducing $\text{Cr}^{3+}(aq)$ to $\text{Cr}^{2+}(aq)$?

46. Consider only the species (at standard conditions)



in answering the following questions. Give reasons for your answers. (Use data from Table 17.1.)

a. Which is the strongest oxidizing agent?

b. Which is the strongest reducing agent?

c. Which species can be oxidized by $\text{SO}_4^{2-}(aq)$ in acid?

d. Which species can be reduced by $\text{Al}(s)$?

47. Use the table of standard reduction potentials (Table 17.1) to pick a reagent that is capable of each of the following oxidations (under standard conditions in acidic solution).

a. Oxidize Br^- to Br_2 but not oxidize Cl^- to Cl_2

b. Oxidize Mn to Mn^{2+} but not oxidize Ni to Ni^{2+}

48. Use the table of standard reduction potentials (Table 17.1) to pick a reagent that is capable of each of the following reductions (under standard conditions in acidic solution).

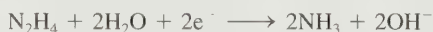
a. Reduce Cu^{2+} to Cu but not reduce Cu^{2+} to Cu^+ .

b. Reduce Br_2 to Br^- but not reduce I_2 to I^- .

49. Hydrazine is somewhat toxic. Use the half-reactions shown below to explain why household bleach (a highly alkaline solution of sodium hypochlorite) should not be mixed with household ammonia or glass cleansers that contain ammonia.



$$\mathcal{E}^\circ = 0.90 \text{ V}$$



$$\mathcal{E}^\circ = -0.10 \text{ V}$$

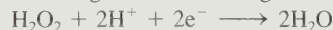
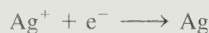
50. The compound with the formula TlI_3 is a black solid. Given the following standard reduction potentials,



would you formulate this compound as thallium(III) iodide or thallium(I) triiodide?

The Nernst Equation

51. A galvanic cell is based on the following half-reactions at 25°C :

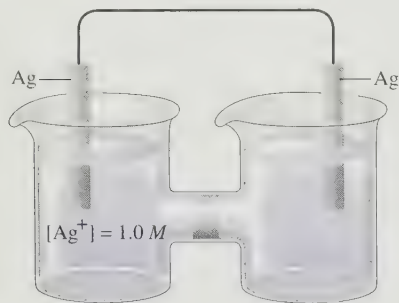


Predict whether $\mathcal{E}_{\text{cell}}$ is larger or smaller than $\mathcal{E}_{\text{cell}}^{\circ}$ for the following cases.

- $[\text{Ag}^+] = 1.0 \text{ M}$, $[\text{H}_2\text{O}_2] = 2.0 \text{ M}$, $[\text{H}^+] = 2.0 \text{ M}$
 - $[\text{Ag}^+] = 2.0 \text{ M}$, $[\text{H}_2\text{O}_2] = 1.0 \text{ M}$, $[\text{H}^+] = 1.0 \times 10^{-7} \text{ M}$
52. Consider the concentration cell in Fig. 17.10. If the Fe^{2+} concentration in the right compartment is changed from 0.1 M to $1 \times 10^{-7} \text{ M}$ Fe^{2+} , predict the direction of electron flow, and designate the anode and cathode compartments.
53. Consider the concentration cell shown below. Calculate the cell potential at 25°C when the concentration of Ag^+ in the compartment on the right is the following.

- 1.0 M
- 2.0 M
- 0.10 M
- $4.0 \times 10^{-5} \text{ M}$
- Calculate the potential when both solutions are 0.10 M in Ag^+ .

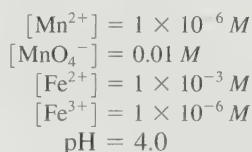
For each case, also identify the cathode, the anode, and the direction in which electrons flow.



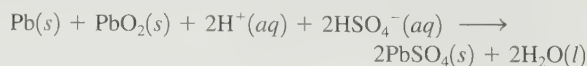
54. Consider a concentration cell similar to the one shown in Exercise 53, except that both electrodes are made of Ni and in the left-hand compartment $[\text{Ni}^{2+}] = 1.0 \text{ M}$. Calculate the cell potential at 25°C when the concentration of Ni^{2+} in the compartment on the right has each of the following values.
- 1.0 M
 - 2.0 M
 - 0.10 M
 - $4.0 \times 10^{-5} \text{ M}$
 - Calculate the potential when both solutions are 2.5 M in Ni^{2+} .

For each case, also identify the cathode, anode, and the direction in which electrons flow.

55. Can permanganate ion oxidize Fe^{2+} to Fe^{3+} at 25°C under the following conditions?



56. The overall reaction in the lead storage battery is



Calculate $\mathcal{E}$ at 25°C for this battery when $[\text{H}_2\text{SO}_4] = 4.5 \text{ M}$, that is, $[\text{H}^+] = [\text{HSO}_4^-] = 4.5 \text{ M}$. At 25°C , $\mathcal{E}^{\circ} = 2.04 \text{ V}$ for the lead storage battery.

57. Consider the cell described below:



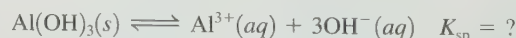
Calculate the cell potential after the reaction has operated long enough for the $[\text{Zn}^{2+}]$ to have changed by 0.20 mol/L . (Assume $T = 25^{\circ}\text{C}$.)

58. Consider the cell described below:



Calculate the cell potential after the reaction has operated long enough for the $[\text{Al}^{3+}]$ to have changed by 0.60 mol/L . (Assume $T = 25^{\circ}\text{C}$.)

59. An electrochemical cell consists of a standard hydrogen electrode and a copper metal electrode.
- What is the potential of the cell at 25°C if the copper electrode is placed in a solution in which $[\text{Cu}^{2+}] = 2.5 \times 10^{-4} \text{ M}$?
 - The copper electrode is placed in a solution of unknown $[\text{Cu}^{2+}]$. The measured potential at 25°C is 0.195 V . What is $[\text{Cu}^{2+}]$? (Assume Cu^{2+} is reduced.)
60. An electrochemical cell consists of a nickel metal electrode immersed in a solution with $[\text{Ni}^{2+}] = 1.0 \text{ M}$ separated by a porous disk from an aluminum metal electrode.
- What is the potential of this cell at 25°C if the aluminum electrode is placed in a solution in which $[\text{Al}^{3+}] = 7.2 \times 10^{-3} \text{ M}$?
 - When the aluminum electrode is placed in a certain solution in which $[\text{Al}^{3+}]$ is unknown, the measured cell potential at 25°C is 1.62 V . Calculate $[\text{Al}^{3+}]$ in the unknown solution. (Assume Al is oxidized.)
61. An electrochemical cell consists of a standard hydrogen electrode and a copper metal electrode. If the copper electrode is placed in a solution of 0.10 M NaOH that is saturated with Cu(OH)_2 , what is the cell potential at 25°C ? (For Cu(OH)_2 , $K_{\text{sp}} = 1.6 \times 10^{-19}$.)
62. An electrochemical cell consists of a nickel metal electrode immersed in a solution with $[\text{Ni}^{2+}] = 1.0 \text{ M}$ separated by a porous disk from an aluminum metal electrode immersed in a solution with $[\text{Al}^{3+}] = 1.0 \text{ M}$. Sodium hydroxide is added to the aluminum compartment causing $\text{Al(OH)}_3\text{(s)}$ to precipitate. After precipitation of Al(OH)_3 has ceased, the concentration of OH^- is $1.0 \times 10^{-4} \text{ M}$ and the measured cell potential is 1.82 V . Calculate the K_{sp} value for Al(OH)_3 .



63. Calculate ΔG° and K at 25°C for the reactions in Exercises 25 and 29.
64. Calculate ΔG° and K at 25°C for the reactions in Exercises 26 and 30.

65. Under standard conditions, what reaction occurs, if any, when each of the following operations are performed?

- Crystals of I_2 are added to a solution of $NaCl$.
- Cl_2 gas is bubbled into a solution of NaI .
- A silver wire is placed in a solution of $CuCl_2$.
- An acidic solution of $FeSO_4$ is exposed to air.

For the reactions that occur, write a balanced equation and calculate $\mathcal{E}^\circ$, ΔG° , and K at $25^\circ C$.

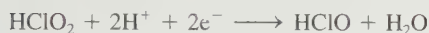
66. A disproportionation reaction involves a substance that acts as both an oxidizing and reducing agent, producing higher and lower oxidation states of the same element in the products. Which of the following disproportionation reactions are spontaneous under standard conditions? Calculate ΔG° and K at $25^\circ C$ for those reactions that are spontaneous under standard conditions.

- $2Cu^+(aq) \rightarrow Cu^{2+}(aq) + Cu(s)$
- $3Fe^{2+}(aq) \rightarrow 2Fe^{3+}(aq) + Fe(s)$
- $HClO_2(aq) \rightarrow ClO_3^-(aq) + HClO(aq)$ (unbalanced)

Use the half-reactions

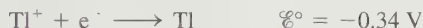


$$\mathcal{E}^\circ = 1.21 \text{ V}$$



$$\mathcal{E}^\circ = 1.65 \text{ V}$$

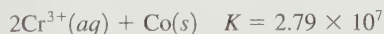
67. Consider the galvanic cell based on the following half-reactions:



- Determine the overall cell reaction and calculate $\mathcal{E}_{\text{cell}}^\circ$.
 - Calculate ΔG° and K for the cell reaction at $25^\circ C$.
 - Calculate $\mathcal{E}_{\text{cell}}$ at $25^\circ C$ when $[Au^{3+}] = 1.0 \times 10^{-2} M$ and $[Tl^+] = 1.0 \times 10^{-4} M$.
68. Consider the following galvanic cell at $25^\circ C$:

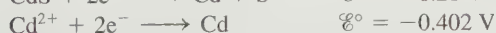
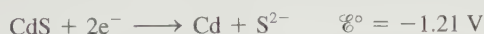


The overall reaction and equilibrium constant value are

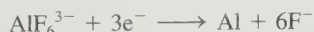


Calculate the cell potential, $\mathcal{E}$, for this galvanic cell and ΔG for the cell reaction at these conditions.

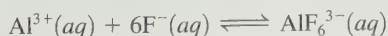
69. Cadmium sulfide (CdS) is used in some semiconductor applications. Calculate the value of the solubility product (K_{sp}) for CdS given the following standard reduction potentials:



70. For the following half-reaction, $\mathcal{E}^\circ = -2.07 \text{ V}$:



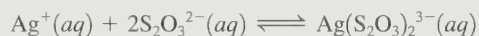
Using data from Table 17.1, calculate the equilibrium constant at $25^\circ C$ for the reaction



71. For the following half-reaction, $\mathcal{E}^\circ = +0.017 \text{ V}$:



Calculate the value of the equilibrium constant at $25^\circ C$ for the following reaction:



(Hint: Find a half-reaction that can be added to the one above to give the required reaction.)

72. The solubility product for $CuI(s)$ is 1.1×10^{-12} . Calculate the value of $\mathcal{E}^\circ$ for the half-reaction



Electrolysis

73. How long will it take to plate out each of the following with a current of 100.0 A ?

- 1.0 kg Al from aqueous Al^{3+}
- 1.0 g Ni from aqueous Ni^{2+}
- 5.0 mol Ag from aqueous Ag^+

74. The electrolysis of BiO^+ produces pure bismuth. How long would it take to produce 10.0 g of Bi by the electrolysis of a BiO^+ solution using a current of 25.0 A ?

75. What mass of each of the following substances can be produced in 1.0 hour with a current of 15 A ?

- Co from aqueous Co^{2+}
- Hf from aqueous Hf^{4+}
- I_2 from aqueous KI
- Cr from molten CrO_3

76. Aluminum is produced commercially by the electrolysis of Al_2O_3 in the presence of a molten salt. If a plant has a continuous capacity of 1.00 million amp , what mass of aluminum can be produced in 2.00 h ?

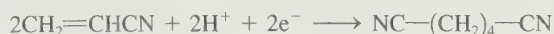
77. Electrolysis of a molten metal chloride (MCl_3) using a current of 6.50 A for 1397 seconds deposits 1.41 g of the metal at the cathode. What is the metal?

78. Electrolysis of an alkaline earth metal chloride using a current of 5.00 A for 748 seconds deposits 0.471 g of metal at the cathode. What is the identity of the alkaline earth metal chloride?

79. What volume of F_2 gas, at $25^\circ C$ and 1.00 atm , is produced when molten KF is electrolyzed by a current of 10.0 A for 2.00 hours ? What mass of potassium metal is produced? At which electrode does each reaction occur?

80. What volumes of $H_2(g)$ and $O_2(g)$ at STP are produced from the electrolysis of water by a current of 2.50 A in 15.0 minutes ?

81. One of the few industrial-scale processes that produce organic compounds electrochemically is used by the Monsanto Company to produce 1,4-dicyanobutane. The reduction reaction is



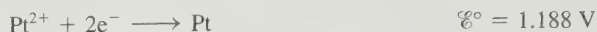
The $\text{NC}-(\text{CH}_2)_4-\text{CN}$ is then chemically reduced using hydrogen gas to $\text{H}_2\text{N}-(\text{CH}_2)_6-\text{NH}_2$, which is used in the production of nylon. What current must be used to produce 150. kg of $\text{NC}-(\text{CH}_2)_4-\text{CN}$ per hour?

82. A single Hall-Heroult cell (as shown in Fig. 17.22) produces about 1 ton of aluminum in 24 hours. What current must be used to accomplish this?
83. It took 2.30 minutes using a current of 2.00 A to plate out all the silver from 0.250 L of a solution containing Ag^+ . What was the original concentration of Ag^+ in the solution?
84. A solution containing Pt^{4+} is electrolyzed with a current of 4.00 A. How long will it take to plate out 99% of the platinum in 0.50 L of a 0.010 M solution of Pt^{4+} ?
85. A solution at 25°C contains 1.0 M Cd^{2+} , 1.0 M Ag^+ , 1.0 M Au^{3+} , and 1.0 M Ni^{2+} in the cathode compartment of an electrolytic cell. Predict the order in which the metals will plate out as the voltage is gradually increased.
86. What reactions occur at the anode and the cathode when an acidic aqueous solution of FeSO_4 is electrolyzed? (Assume standard conditions.)
87. What reactions take place at the cathode and the anode when each of the following is electrolyzed?
- molten NiBr_2
 - molten AlF_3
 - molten MnI_2
88. What reactions take place at the cathode and the anode when each of the following is electrolyzed? (Assume standard conditions.)
- 1.0 M NiBr_2 solution
 - 1.0 M AlF_3 solution
 - 1.0 M MnI_2 solution

Additional Exercises

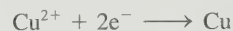
89. The saturated calomel electrode, abbreviated SCE, is often used as a reference electrode in making electrochemical measurements. The SCE is composed of mercury in contact with a saturated solution of calomel (Hg_2Cl_2). The electrolyte solution is saturated KCl. $\mathcal{E}_{\text{SCE}}$ is +0.242 V relative to the standard hydrogen electrode. Calculate the potential for each of the following galvanic cells containing a saturated calomel electrode and the given half-cell components at standard conditions. In each case, indicate whether the SCE is the cathode or the anode. Standard reduction potentials are found in Table 17.1.
- $\text{Cu}^{2+} + 2\text{e}^- \longrightarrow \text{Cu}$
 - $\text{Fe}^{3+} + \text{e}^- \longrightarrow \text{Fe}^{2+}$
 - $\text{AgCl} + \text{e}^- \longrightarrow \text{Ag} + \text{Cl}^-$
 - $\text{Al}^{3+} + 3\text{e}^- \longrightarrow \text{Al}$
 - $\text{Ni}^{2+} + 2\text{e}^- \longrightarrow \text{Ni}$

90. Consider the following half-reactions:



Explain why platinum metal will dissolve in aqua regia (a mixture of hydrochloric and nitric acids) but not in either concentrated nitric or concentrated hydrochloric acid individually.

91. Consider the standard galvanic cell based on the following half-reactions



The electrodes in this cell are Ag(s) and Cu(s) . Does the cell potential increase, decrease, or remain the same when the following changes occur to the standard cell?

- $\text{CuSO}_4(\text{s})$ is added to the copper half-cell compartment (assume no volume change).
- $\text{NH}_3(\text{aq})$ is added to the copper half-cell compartment. *Hint:* Cu^{2+} reacts with NH_3 to form $\text{Cu}(\text{NH}_3)_4^{2+}(\text{aq})$.
- NaCl(s) is added to the silver half-cell compartment. *Hint:* Ag^+ reacts with Cl^- to form AgCl(s) .
- Water is added to both half-cell compartments until the volume of solution is doubled.
- The silver electrode is replaced with a platinum electrode.

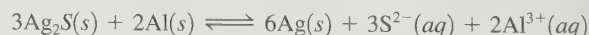


92. A standard galvanic cell is constructed so that the overall cell reaction is

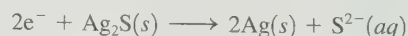


where M is an unknown metal. If $\Delta G^\circ = -411 \text{ kJ}$ for the overall cell reaction, identify the metal used to construct the standard cell.

93. The black silver sulfide discoloration of silverware can be removed by heating the silver article in a sodium carbonate solution in an aluminum pan. The reaction is



- Using data in Appendix 4, calculate ΔG° , K , and $\mathcal{E}^\circ$ for the above reaction at 25°C. (For $\text{Al}^{3+}(\text{aq})$, $\Delta G_f^\circ = -480. \text{ kJ/mol.}$)
- Calculate the value of the standard reduction potential for the following half-reaction:



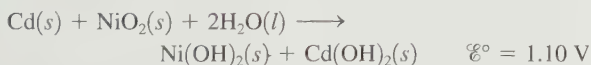
94. In 1973 the wreckage of the Civil War ironclad USS *Monitor* was discovered near Cape Hatteras, North Carolina. (The *Monitor* and the CSS *Virginia* [formerly the USS *Merri-mack*] fought the first battle between iron-armored ships.) In 1987 investigations were begun to see if the ship could be salvaged. It was reported in *Time* (June 22, 1987) that sci-

entists were considering adding sacrificial anodes of zinc to the rapidly corroding metal hull of the *Monitor*. Describe how attaching zinc to the hull would protect the *Monitor* from further corrosion.

95. A cleaning solution for glassware is prepared by dissolving potassium dichromate in concentrated sulfuric acid. [This solution is much less commonly used because of the carcinogenic properties of chromium(VI) compounds.] An unthinking chemist tried to prepare some cleaning solution from some waste potassium dichromate that had been contaminated by sodium chloride. On adding the solid to some sulfuric acid, he was driven from the lab by pungent fumes. What happened?
96. When aluminum foil is placed in hydrochloric acid, nothing happens for the first 30 seconds or so. This is followed by vigorous bubbling and the eventual disappearance of the foil. Explain these observations.
97. A patent attorney has asked for your advice concerning the merits of a patent application that describes a single aqueous galvanic cell capable of producing a 12-V potential. Comment.
98. The overall reaction and equilibrium constant value for a hydrogen-oxygen fuel cell at 298 K is



- a. Calculate $\mathcal{E}^\circ$ and ΔG° at 298 K for the fuel cell reaction.
- b. Predict the signs of ΔH° and ΔS° for the fuel cell reaction.
- c. As temperature increases, does the maximum amount of work obtained from the fuel cell reaction increase, decrease, or remain the same? Explain.
99. What is the maximum work that can be obtained from a hydrogen-oxygen fuel cell at standard conditions that produces 1.00 kg of water at 25°C? Why do we say that this is the maximum work that can be obtained? What are the advantages and disadvantages in using fuel cells rather than the corresponding combustion reactions to produce electricity?
100. The overall reaction and standard cell potential at 25°C for the rechargeable nickel-cadmium alkaline battery is



For every mole of Cd consumed in the cell, what is the maximum useful work that can be obtained at standard conditions?

101. An experimental fuel cell has been designed that uses carbon monoxide as fuel. The overall reaction is



The two half-cell reactions are



The two half-reactions are carried out in separate compartments connected with a solid mixture of CeO_2 and Gd_2O_3 . Oxide ions can move through this solid at high temperatures

(about 800°C). ΔG for the overall reaction at 800°C under certain concentration conditions is -380 kJ . Calculate the cell potential for this fuel cell at the same temperature and concentration conditions.

102. In the electrolysis of a sodium chloride solution, what volume of $\text{H}_2(\text{g})$ is produced in the same time it takes to produce 257 L of $\text{Cl}_2(\text{g})$, with both volumes measured at 50.°C and 2.50 atm?
103. An aqueous solution of an unknown salt of ruthenium is electrolyzed by a current of 2.50 A passing for 50.0 minutes. If 2.618 g Ru is produced at the cathode, what is the charge on the ruthenium ions in solution?
104. It takes 15 kWh (kilowatt-hours) of electrical energy to produce 1.0 kg of aluminum metal from aluminum oxide by the Hall-Heroult process. Compare this to the amount of energy necessary to melt 1.0 kg of aluminum metal. Why is it economically feasible to recycle aluminum cans? (The enthalpy of fusion for aluminum metal is 10.7 kJ/mol [1 watt = 1 J/s].)

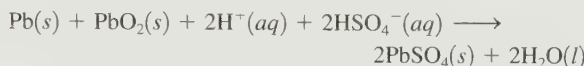
Challenge Problems

105. Combine the equations

$$\Delta G^\circ = -nF\mathcal{E}^\circ \quad \text{and} \quad \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

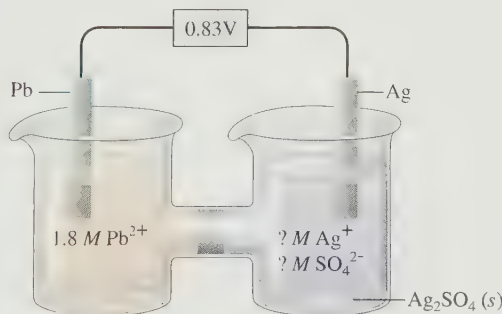
to derive an expression for $\mathcal{E}^\circ$ as a function of temperature. Describe how one can graphically determine ΔH° and ΔS° from measurements of $\mathcal{E}^\circ$ at different temperatures, assuming that ΔH° and ΔS° do not depend on temperature. What property would you look for in designing a reference half-cell that would produce a potential relatively stable with respect to temperature?

106. The overall reaction in the lead storage battery is



- a. For the cell reaction $\Delta H^\circ = -315.9 \text{ kJ}$ and $\Delta S^\circ = 263.5 \text{ J/K}$. Calculate $\mathcal{E}^\circ$ at $-20.^\circ\text{C}$. Assume ΔH° and ΔS° do not depend on temperature.
- b. Calculate $\mathcal{E}$ at $-20.^\circ\text{C}$ when $[\text{HSO}_4^-] = [\text{H}^+] = 4.5 \text{ M}$.
- c. Consider your answer to Exercise 56. Why does it seem that batteries fail more often on cold days than on warm days?

107. Consider the following galvanic cell:



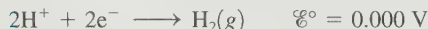
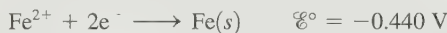
Calculate the K_{sp} value for $\text{Ag}_2\text{SO}_4(s)$. Note that to obtain silver ions in the right compartment (the cathode compartment), excess solid Ag_2SO_4 was added and some of the salt dissolved.

108. A zinc–copper battery is constructed as follows at 25°C:



The mass of each electrode is 200. g.

- Calculate the cell potential when this battery is first connected.
 - Calculate the cell potential after 10.0 A of current has flowed for 10.0 h. (Assume each half-cell contains 1.00 L of solution.)
 - Calculate the mass of each electrode after 10.0 h.
 - How long can this battery deliver a current of 10.0 A before it goes dead?
109. A galvanic cell is based on the following half-reactions:

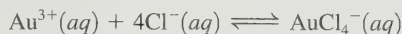


where the iron compartment contains an iron electrode and $[\text{Fe}^{2+}] = 1.00 \times 10^{-3}\text{ M}$ and the hydrogen compartment contains a platinum electrode, $P_{\text{H}_2} = 1.00\text{ atm}$, and a weak acid, HA, at an initial concentration of 1.00 M. If the observed cell potential is 0.333 V at 25°C, calculate the K_a value for the weak acid HA.

110. Consider a cell based on the following half-reactions:



- Draw this cell under standard conditions, labeling the anode, the cathode, the direction of electron flow, and the concentrations, as appropriate.
- When enough $\text{NaCl}(s)$ is added to the compartment containing gold to make the $[\text{Cl}^-] = 0.10\text{ M}$, the cell potential is observed to be 0.31 V. Assume that Au^{3+} is reduced and assume that the reaction in the compartment containing gold is



Calculate the value of K for this reaction at 25°C.

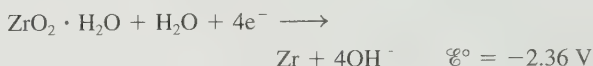
111. The measurement of pH using a glass electrode obeys the Nernst equation. The typical response of a pH meter at 25.00°C is given by the equation

$$\mathcal{E}_{\text{meas}} = \mathcal{E}_{\text{ref}} + 0.05916\text{ pH}$$

where $\mathcal{E}_{\text{ref}}$ contains the potential of the reference electrode and all other potentials that arise in the cell that are not related to the hydrogen ion concentration. Assume that $\mathcal{E}_{\text{ref}} = 0.250\text{ V}$ and that $\mathcal{E}_{\text{meas}} = 0.480\text{ V}$.

- What is the uncertainty in the values of pH and $[\text{H}^+]$ if the uncertainty in the measured potential is $\pm 1\text{ mV}$ ($\pm 0.001\text{ V}$)?
- To what accuracy must the potential be measured for the uncertainty in pH to be $\pm 0.02\text{ pH unit}$?

112. Zirconium is one of the few metals that retains its structural integrity upon exposure to radiation. For this reason, the fuel rods in most nuclear reactors are made of zirconium. Answer the following questions about the redox properties of zirconium based on the half-reaction



- Is zirconium metal capable of reducing water to form hydrogen gas at standard conditions?
- Write a balanced equation for the reduction of water by zirconium metal.
- Calculate $\mathcal{E}^\circ$, ΔG° , and K for the reduction of water by zirconium metal.
- The reduction of water by zirconium occurred during the accident at Three Mile Island, Pennsylvania, in 1979. The hydrogen produced was successfully vented and no chemical explosion occurred. If $1.00 \times 10^3\text{ kg}$ of Zr reacts, what mass of H_2 is produced? What volume of H_2 at 1.0 atm and 1000.°C is produced?
- At Chernobyl, USSR, in 1986, hydrogen was produced by the reaction of superheated steam with the graphite reactor core:



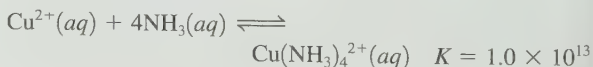
A chemical explosion involving the hydrogen gas did occur at Chernobyl. In light of this fact, do you think it was a correct decision to vent the hydrogen and other radioactive gases into the atmosphere at Three Mile Island? Explain.

113. A galvanic cell is based on the following half-reactions:



In this cell, the silver compartment contains a silver electrode and excess $\text{AgCl}(s)$ ($K_{sp} = 1.6 \times 10^{-10}$), and the copper compartment contains a copper electrode and $[\text{Cu}^{2+}] = 2.0\text{ M}$.

- Calculate the potential for this cell at 25°C.
- Assuming 1.0 L of 2.0 M Cu^{2+} in the copper compartment, calculate the moles of NH_3 that would have to be added to give a cell potential of 0.52 V at 25°C (assume no volume change on addition of NH_3).



Marathon Problem*

This problem is designed to incorporate several concepts and techniques into one situation. Marathon Problems can be used in class by groups of students to help facilitate problem-solving skills.

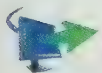
114. The addition of aqueous ammonia to the cathode compartment of the cell described below reduces the cell potential. Likewise, addition of aqueous ammonia to the anode compartment increases the cell potential.



Assume that $[\text{Cu}^{2+}(aq)]_0 = [\text{Zn}^{2+}(aq)]_0 = 0.10\text{ M}$ and that both Cu^{2+} and Zn^{2+} form very stable complexes with ammonia (overall formation constants $> 10^{10}$), each with a coordination number of 4.

- Show how to estimate the ratio of the overall formation constant for $[\text{Zn}(\text{NH}_3)_4]^{2+}$ to the overall formation constant for $[\text{Cu}(\text{NH}_3)_4]^{2+}$ if the cell potential is observed to be 0.96 V after adding equal amounts (assume a large excess) of 6 M NH_3 to each compartment (assume that $T = 298\text{ K}$).
- Which of the two transition metal complexes is more thermodynamically stable? How much more stable is it than the other complex?

- What is the purpose of the salt bridge? Cations in a salt bridge always flow to the cathode, whereas anions in a salt bridge always flow to the anode. In terms of the zinc-tin galvanic cell illustrated in the activity, explain why this is the case. Which way do electrons always flow in a galvanic cell?
 - Standard reduction potentials are determined relative to some standard. What is the standard?
 - Given two reduction potentials to design a galvanic cell, how do you determine which is the reduction half-reaction and which is the oxidation half-reaction?
 - For additional review material on galvanic cells, open the Galvanic Cells Visualization on the student CD.
- To see an example of an electrolytic cell, open the Electrolysis of Water Visualization on the student CD.
 - What half-reactions are occurring at the anode and the cathode? (*Hint:* Review Table 17.1 in your text.)
 - What gas was produced on the right side of the apparatus? On the left side? The volume of gases produced are a ratio of about 2:1. Does this make sense? (*Hint:* Determine the overall reaction occurring when water is electrolyzed.)
 - Compare and contrast electrolytic cells and galvanic cells. What are some uses of electrolytic processes?
 - Test your understanding of Chapter 17 material by taking the ACE quizzes on the student web site.



Media Activities

- Open the Electrochemistry Understanding Concepts activity on the student CD and go through the introduction and examples to review redox reactions and galvanic (voltaic) cells.



For additional web activities and other resources, visit the Zumdahl, *Chemistry*, Sixth Edition textbook site at <http://chemistry.college.hmco.com/students>.

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The Nucleus: A Chemist's View

Since the chemistry of an atom is determined by the number and arrangement of its electrons, the properties of the nucleus are not of primary importance to chemists. In the simplest view, the nucleus provides the positive charge to bind the electrons in atoms and molecules. However, a quick reading of any daily newspaper will show you that the nucleus and its properties have an important impact on our society. This chapter considers those aspects of the nucleus about which everyone should have some knowledge.

Several aspects of the nucleus are immediately impressive: its very small size, its very large density, and the magnitude of the energy that holds it together. The radius of a typical nucleus appears to be about 10^{-13} cm. This can be compared to the radius of a typical atom, which is on the order of 10^{-8} cm. A visualization will help you appreciate the small size of the nucleus: If the nucleus of the hydrogen atom were the size of a Ping-Pong ball, the electron in the 1s orbital would be, on average, 0.5 kilometer (0.3 mile) away. The density of the nucleus is equally impressive—approximately 1.6×10^{14} g/cm³. A sphere of nuclear material the size of a Ping-Pong ball would have a mass of 2.5 *billion tons*! In addition, the energies involved in nuclear processes are typically millions of times larger than those associated with normal chemical reactions. This fact makes nuclear processes very attractive for feeding the voracious energy appetite of our civilization.

Atomos, the Greek root of the word *atom*, means “indivisible.” It was originally believed that the atom was the ultimate indivisible particle of which all matter was composed. However, as we discussed in Chapter 2, Lord Rutherford showed in 1911 that the atom is not homogeneous, but rather has a dense, positively charged center surrounded by electrons. Subsequently, scientists have learned that the nucleus of the atom can be subdivided into particles called **neutrons** and **protons**. In fact, in the past two decades it has

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 - Types of Radioactive Decay
- 18.2 The Kinetics of Radioactive Decay**
 - Half-Life
- 18.3 Nuclear Transformations**
- 18.4 Detection and Uses of Radioactivity**
 - Dating by Radioactivity
 - Medical Applications of Radioactivity
- 18.5 Thermodynamic Stability of the Nucleus**
- 18.6 Nuclear Fission and Nuclear Fusion**
 - Nuclear Fission
 - Nuclear Reactors
 - Breeder Reactors
 - Fusion
- 18.7 Effects of Radiation**

Workers inside a giant chamber at the National Ignition Facility in California. This chamber will be used to induce nuclear fusion by aiming 192 lasers at a pellet of fuel.

The atomic number Z is the number of protons in a nucleus; the mass number A is the sum of protons and neutrons in a nucleus.

The term *isotopes* refers to a group of nuclides with the same atomic number. Each individual atom is properly called a *nuclide*, not an isotope.

become apparent that even the protons and neutrons are composed of smaller particles called *quarks*.

For most purposes, the nucleus can be regarded as a collection of **nuclcons** (neutrons and protons), and the internal structures of these particles can be ignored. As we discussed in Chapter 2, the number of protons in a particular nucleus is called the **atomic number** (Z), and the sum of the neutrons and protons is the **mass number** (A). Atoms that have identical atomic numbers but different mass number values are called **isotopes**. However, we usually do not use the singular form *isotope* to refer to a particular member of a group of isotopes. Rather, we use the term *nuclide*. A **nuclide** is a unique atom, represented by the symbol

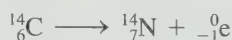


where X represents the symbol for a particular element. For example, the following nuclides constitute the isotopes of carbon: carbon-12 (${}^{12}_6\text{C}$), carbon-13 (${}^{13}_6\text{C}$), and carbon-14 (${}^{14}_6\text{C}$).

18.1 Nuclear Stability and Radioactive Decay

Nuclear stability is the central topic of this chapter and forms the basis for all the important applications related to nuclear processes. Nuclear stability can be considered from both a kinetic and a thermodynamic point of view. **Thermodynamic stability**, as we will use the term here, refers to the potential energy of a particular nucleus as compared with the sum of the potential energies of its component protons and neutrons. We will use the term **kinetic stability** to describe the probability that a nucleus will undergo decomposition to form a different nucleus—a process called **radioactive decay**. We will consider radioactivity in this section.

Many nuclei are radioactive; that is, they decompose, forming another nucleus and producing one or more particles. An example is carbon-14, which decays as follows:



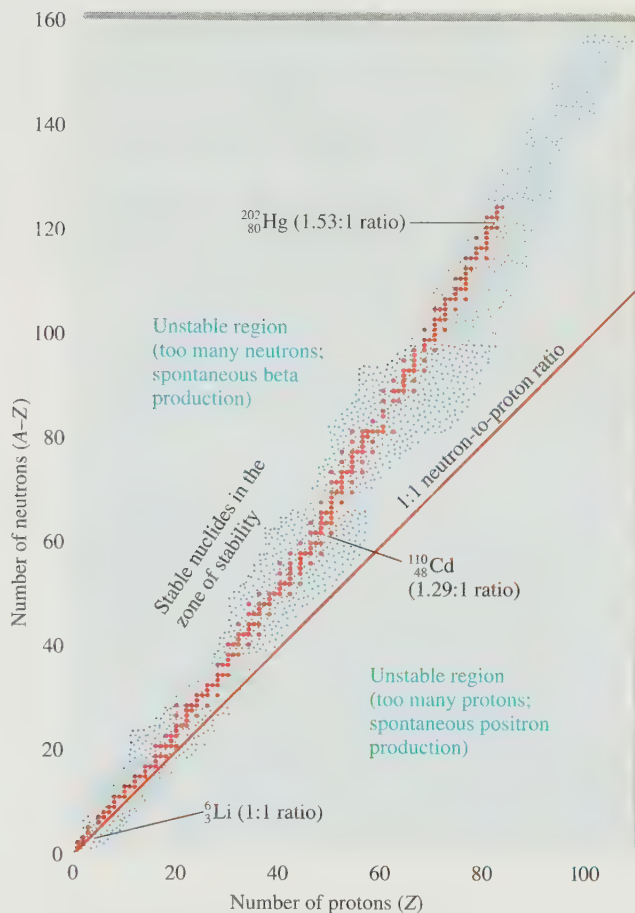
where ${}^0_{-1}\text{e}$ represents an electron, which is called a **beta particle**, or **β particle**, in nuclear terminology. This equation is typical of those representing radioactive decay in that both A and Z must be conserved. That is, the Z values must give the same sum on both sides of the equation ($6 = 7 - 1$), as must the A values ($14 = 14 + 0$).

Of the approximately 2000 known nuclides, only 279 are stable with respect to radioactive decay. Tin has the largest number of stable isotopes—10.

It is instructive to examine how the numbers of neutrons and protons in a nucleus are related to its stability with respect to radioactive decay. Figure 18.1 shows a plot of the positions of the stable nuclei as a function of the number of protons (Z) and the number of neutrons ($A - Z$). The stable nuclides are said to reside in the **zone of stability**.

The following are some important observations concerning radioactive decay:

- All nuclides with 84 or more protons are unstable with respect to radioactive decay.
- Light nuclides are stable when Z equals $A - Z$, that is, when the neutron/proton ratio is 1. However, for heavier elements the neutron/proton ratio required for stability is greater than 1 and increases with Z .

**FIGURE 18.1**

The zone of stability. The red dots indicate the nuclides that *do not* undergo radioactive decay. Note that as the number of protons in a nuclide increases, the neutron/proton ratio required for stability also increases.

- Certain combinations of protons and neutrons seem to confer special stability. For example, nuclides with even numbers of protons and neutrons are more often stable than those with odd numbers, as shown by the data in Table 18.1.
- There are also certain specific numbers of protons or neutrons that produce especially stable nuclides. These *magic numbers* are 2, 8, 20, 28, 50, 82, and 126. This behavior parallels that for atoms in which certain numbers of electrons (2, 10, 18, 36, 54, and 86) produce special chemical stability (the noble gases).

TABLE 18.1 Number of Stable Nuclides Related to Numbers of Protons and Neutrons

Number of Protons	Number of Neutrons	Number of Stable Nuclides	Examples
Even	Even	168	$^{12}_6\text{C}$, $^{16}_8\text{O}$
Even	Odd	57	$^{13}_6\text{C}$, $^{47}_{22}\text{Ti}$
Odd	Even	50	$^{19}_9\text{F}$, $^{23}_{11}\text{Na}$
Odd	Odd	4	^2_1H , ^6_3Li

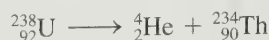
Note: Even numbers of protons and neutrons seem to favor stability.

Types of Radioactive Decay

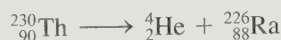
Radioactive nuclei can undergo decomposition in various ways. These decay processes fall into two categories: those that involve a change in the mass number of the decaying nucleus and those that do not. We will consider the former type of process first.

α -particle production involves a change in A for the decaying nucleus; β -particle production has no effect on A .

An **alpha particle**, or α particle, is a helium nucleus (${}^4_2\text{He}$). **Alpha-particle production** is a very common mode of decay for heavy radioactive nuclides. For example, ${}^{238}_{92}\text{U}$, the predominant (99.3%) isotope of natural uranium, decays by α -particle production:

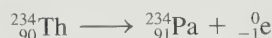


Another α -particle producer is ${}^{230}_{90}\text{Th}$:

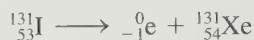


Another decay process in which the mass number of the decaying nucleus changes is **spontaneous fission**, the splitting of a heavy nuclide into two lighter nuclides with similar mass numbers. Although this process occurs at an extremely slow rate for most nuclides, it is important in some cases, such as for ${}^{254}_{98}\text{Cf}$, where spontaneous fission is the predominant mode of decay.

The most common decay process in which the mass number of the decaying nucleus remains constant is **β -particle production**. For example, the thorium-234 nuclide produces a β particle and is converted to protactinium-234:



Iodine-131 is also a β -particle producer:



The β particle is assigned the mass number 0, since its mass is tiny compared with that of a proton or neutron. Because the value of Z is -1 for the β particle, the atomic number for the new nuclide is greater by 1 than for the original nuclide. Thus *the net effect of β -particle production is to change a neutron to a proton*. We therefore expect nuclides that lie above the zone of stability (those nuclides whose neutron/proton ratios are too high) to be β -particle producers.

It should be pointed out that although the β particle is an electron, the emitting nucleus does not contain electrons. As we shall see later in this chapter, a given quantity of energy (which is best regarded as a form of matter) can become a particle (another form of matter) under certain circumstances. The unstable nuclide creates an electron as it releases energy in the decay process. The electron thus results from the decay process rather than being present before the decay occurs. Think of this as somewhat like talking: Words are not stored inside us but are formed as we speak. Later in this chapter we will discuss in more detail this very interesting phenomenon where matter in the form of particles and matter in the form of energy can interchange.

A **gamma ray**, or γ ray, refers to a high-energy photon. Frequently, γ -ray production accompanies nuclear decays and particle reactions, such as in the α -particle decay of ${}^{238}_{92}\text{U}$:

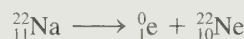


where two γ rays of different energies are produced in addition to the α particle. The emission of γ rays is one way a nucleus with excess energy (in an excited nuclear state) can relax to its ground state.

TABLE 18.2 Various Types of Radioactive Processes Showing the Changes That Take Place in the Nuclides

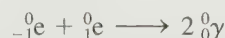
Process	Change in A	Change in Z	Change in Neutron/Proton Ratio	Example
β -particle (electron) production	0	+1	Decrease	${}^{227}_{89}\text{Ac} \longrightarrow {}^{227}_{90}\text{Th} + {}^0_{-1}\text{e}$
Positron production	0	-1	Increase	${}^{13}_7\text{N} \longrightarrow {}^{13}_6\text{C} + {}^0_1\text{e}$
Electron capture	0	-1	Increase	${}^{73}_{33}\text{As} + {}^0_{-1}\text{e} \longrightarrow {}^{73}_{32}\text{Ge}$
α -particle production	-4	-2	Increase	${}^{210}_{84}\text{Po} \longrightarrow {}^{206}_{82}\text{Pb} + {}^4_2\text{He}$
γ -ray production	0	0	—	Excited nucleus $\longrightarrow$ ground state nucleus + ${}^0_0\gamma$
Spontaneous fission	—	—	—	${}^{254}_{98}\text{Cf} \longrightarrow$ lighter nuclides + neutrons

Positron production occurs for nuclides that are below the zone of stability (those nuclides whose neutron/proton ratios are too small). The positron is a particle with the same mass as the electron but opposite charge. An example of a nuclide that decays by positron production is sodium-22:



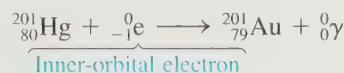
Note that *the net effect is to change a proton to a neutron*, causing the product nuclide to have a higher neutron/proton ratio than the original nuclide.

Besides being oppositely charged, the positron shows an even more fundamental difference from the electron: It is the *antiparticle* of the electron. When a positron collides with an electron, the particulate matter is changed to electromagnetic radiation in the form of high-energy photons:



This process, which is characteristic of matter–antimatter collisions, is called *annihilation* and is another example of the interchange of the forms of matter.

Electron capture is a process in which one of the inner-orbital electrons is captured by the nucleus, as illustrated by the process



This reaction would have been of great interest to the alchemists, but unfortunately it does not occur at a rate that would make it a practical means for changing mercury to gold. Gamma rays are always produced along with electron capture to release excess energy. The various types of radioactive decay are summarized in Table 18.2.

SAMPLE EXERCISE 18.1

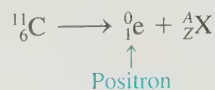
Nuclear Equations I

Write balanced equations for each of the following processes.

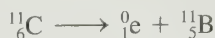
- ${}^{11}_6\text{C}$ produces a positron.
- ${}^{214}_{83}\text{Bi}$ produces a β particle.
- ${}^{237}_{93}\text{Np}$ produces an α particle.

SOLUTION

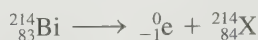
- a. We must find the product nuclide represented by ${}^A_Z\text{X}$ in the following equation:



We can find the identity of ${}^A_Z\text{X}$ by recognizing that the total of the Z and A values must be the same on both sides of the equation. Thus for X , Z must be $6 - 1 = 5$ and A must be $11 - 0 = 11$. Therefore, ${}^A_Z\text{X}$ is ${}^{11}_5\text{B}$. (The fact that Z is 5 tells us that the nuclide is boron.) Thus the balanced equation is

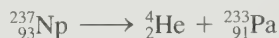


- b. Knowing that a β particle is represented by ${}^0_{-1}\text{e}$ and that Z and A are conserved, we can write



so ${}^A_Z\text{X}$ must be ${}^{214}_{84}\text{Po}$.

- c. Since an α particle is represented by ${}^4_2\text{He}$, the balanced equation must be



See Exercises 18.9 and 18.10.

SAMPLE EXERCISE 18.2

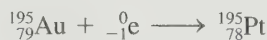
Nuclear Equations II

In each of the following nuclear reactions, supply the missing particle.

- a. ${}^{195}_{79}\text{Au} + ? \rightarrow {}^{195}_{78}\text{Pt}$
 b. ${}^{38}_{19}\text{K} \rightarrow {}^{38}_{18}\text{Ar} + ?$

SOLUTION

- a. Since A does not change and Z decreases by 1, the missing particle must be an electron:



This is an example of electron capture.

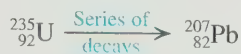
- b. To conserve Z and A , the missing particle must be a positron:



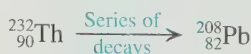
Thus potassium-38 decays by positron production.

See Exercises 18.11 and 18.12.

Often a radioactive nucleus cannot reach a stable state through a single decay process. In such a case, a **decay series** occurs until a stable nuclide is formed. A well-known example is the decay series that starts with ${}^{238}_{92}\text{U}$ and ends with ${}^{206}_{82}\text{Pb}$, as shown in Fig. 18.2. Similar series exist for ${}^{235}_{92}\text{U}$:



and for ${}^{232}_{90}\text{Th}$:



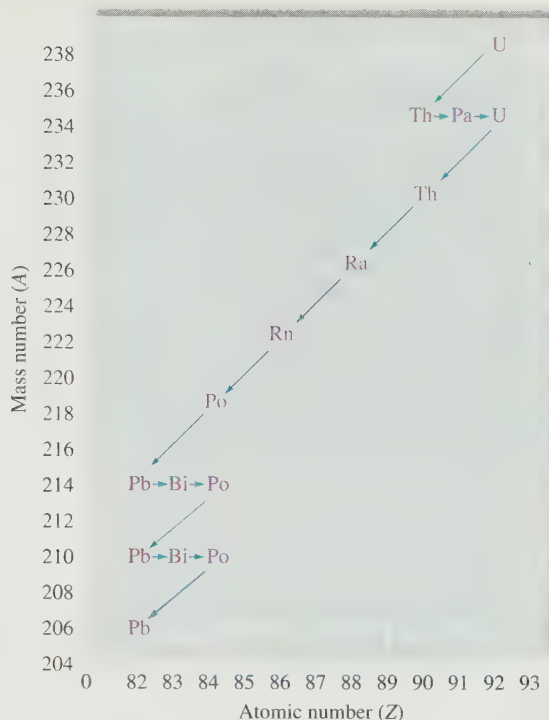


FIGURE 18.2

The decay series from $^{238}_{92}\text{U}$ to $^{206}_{82}\text{Pb}$. Each nuclide in the series except $^{206}_{82}\text{Pb}$ is unstable, and the successive transformations (shown by the arrows) continue until $^{206}_{82}\text{Pb}$ is finally formed. Note that horizontal arrows indicate processes where A is unchanged, while diagonal arrows signify that both A and Z change.

18.2 The Kinetics of Radioactive Decay

In a sample containing radioactive nuclides of a given type, each nuclide has a certain probability of undergoing decay. Suppose that a sample of 1000 atoms of a certain nuclide produces 10 decay events per hour. This means that over the span of an hour, 1 out of every 100 nuclides will decay. Given that this probability of decay is characteristic for this type of nuclide, we could predict that a 2000-atom sample would give 20 decay events per hour. Thus, for radioactive nuclides, the **rate of decay**, which is the negative of the change in the number of nuclides per unit time

$$\left(-\frac{\Delta N}{\Delta t} \right)$$

is directly proportional to the number of nuclides N in a given sample:

$$\text{Rate} = -\frac{\Delta N}{\Delta t} \propto N$$

The negative sign is included because the number of nuclides is decreasing. We now insert a proportionality constant k to give

$$\text{Rate} = -\frac{\Delta N}{\Delta t} = kN$$

This is the rate law for a first-order process, as we saw in Chapter 12. As shown in Section 12.4, the integrated first-order rate law is

$$\ln \left(\frac{N}{N_0} \right) = -kt$$

where N_0 represents the original number of nuclides (at $t = 0$) and N represents the number *remaining* at time t .

Rates of reaction are discussed in Chapter 12.

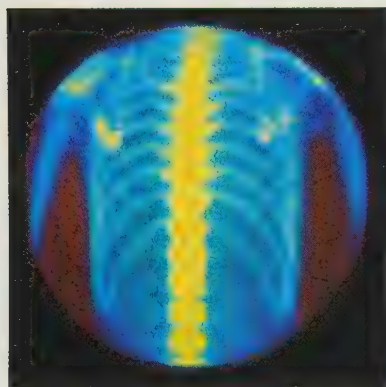
Half-Life

The **half-life** ($t_{1/2}$) of a radioactive sample is defined as the time required for the number of nuclides to reach half the original value ($N_0/2$). We can use this definition in connection with the integrated first-order rate law (as we did in Section 12.4) to produce the following expression for $t_{1/2}$:

$$t_{1/2} = \frac{\ln(2)}{k} = \frac{0.693}{k}$$

Thus, if the half-life of a radioactive nuclide is known, the rate constant can be easily calculated, and vice versa.

SAMPLE EXERCISE 18.3



The image of a bone scan of a normal chest (posterior view). Radioactive technetium-99m is injected into the patient and is then concentrated in bones, allowing a physician to look for abnormalities such as might be caused by cancer.

The harmful effects of radiation will be discussed in Section 18.7.

Kinetics of Nuclear Decay I

Technetium-99m is used to form pictures of internal organs in the body and is often used to assess heart damage. The *m* for this nuclide indicates an excited nuclear state that decays to the ground state by gamma emission. The rate constant for decay of $^{99m}_{43}\text{Tc}$ is known to be $1.16 \times 10^{-1}/\text{h}$. What is the half-life of this nuclide?

SOLUTION

The half-life can be calculated from the expression

$$\begin{aligned} t_{1/2} &= \frac{0.693}{k} = \frac{0.693}{1.16 \times 10^{-1}/\text{h}} \\ &= 5.98 \text{ h} \end{aligned}$$

Thus it will take 5.98 h for a given sample of technetium-99m to decrease to half the original number of nuclides.

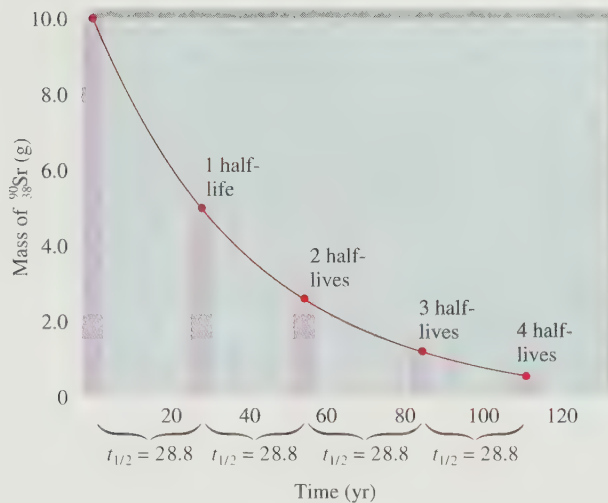
See Exercise 18.19.

As we saw in Section 12.4, the half-life for a first-order process is constant. This is shown for the β -particle decay of strontium-90 in Fig. 18.3; it takes 28.8 years for each halving of the amount of $^{90}_{38}\text{Sr}$. Contamination of the environment with $^{90}_{38}\text{Sr}$ poses serious health hazards because of the similar chemistry of strontium and calcium (both are in Group 2A). Strontium-90 in grass and hay is incorporated into cow's milk along with calcium and is then passed on to humans, where it lodges in the bones. Because of its relatively long half-life, it persists for years in humans, causing radiation damage that may lead to cancer.

SAMPLE EXERCISE 18.4

Kinetics of Nuclear Decay II

The half-life of molybdenum-99 is 67.0 h. How much of a 1.000-mg sample of $^{99}_{42}\text{Mo}$ is left after 335 h?

**FIGURE 18.3**

The decay of a 10.0-g sample of strontium-90 over time. Note that the half-life is a constant 28.8 years.

SOLUTION

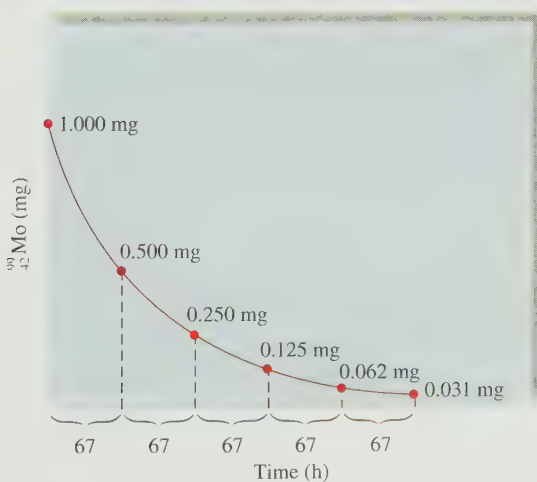
The easiest way to solve this problem is to recognize that 335 h represents five half-lives for $^{99}_{42}\text{Mo}$:

$$335 = 5 \times 67.0$$

We can sketch the change that occurs, as is shown in Fig. 18.4. Thus, after 335 h, 0.031 mg $^{99}_{42}\text{Mo}$ remains.

See Exercise 18.21.

The half-lives of radioactive nuclides vary over a tremendous range. For example, $^{144}_{60}\text{Nd}$ has a half-life of 5×10^{15} years, while $^{214}_{84}\text{Po}$ has a half-life of 2×10^{-4} second. To give you some perspective on this, the half-lives of the nuclides in the $^{238}_{92}\text{U}$ decay series are given in Table 18.3.

**FIGURE 18.4**

The change in the amount of $^{99}_{42}\text{Mo}$ with time ($t_{1/2} = 67$ h).

TABLE 18.3 The Half-Lives of Nuclides in the $^{238}_{92}\text{U}$ Decay Series

Nuclide	Particle Produced	Half-Life
Uranium-238 ($^{238}_{92}\text{U}$)	α	4.51×10^9 years
↓		
Thorium-234 ($^{234}_{90}\text{Th}$)	β	24.1 days
↓		
Protactinium-234 ($^{234}_{91}\text{Pa}$)	β	6.75 hours
↓		
Uranium-234 ($^{234}_{92}\text{U}$)	α	2.48×10^5 years
↓		
Thorium-230 ($^{230}_{90}\text{Th}$)	α	8.0×10^4 years
↓		
Radium-226 ($^{226}_{88}\text{Ra}$)	α	1.62×10^3 years
↓		
Radon-222 ($^{222}_{86}\text{Rn}$)	α	3.82 days
↓		
Polonium-218 ($^{218}_{84}\text{Po}$)	α	3.1 minutes
↓		
Lead-214 ($^{214}_{82}\text{Pb}$)	β	26.8 minutes
↓		
Bismuth-214 ($^{214}_{83}\text{Bi}$)	β	19.7 minutes
↓		
Polonium-214 ($^{214}_{84}\text{Po}$)	α	1.6×10^{-4} second
↓		
Lead-210 ($^{210}_{82}\text{Pb}$)	β	20.4 years
↓		
Bismuth-210 ($^{210}_{83}\text{Bi}$)	β	5.0 days
↓		
Polonium-210 ($^{210}_{84}\text{Po}$)	α	138.4 days
↓		
Lead-206 ($^{206}_{82}\text{Pb}$)	—	Stable

18.3 Nuclear Transformations

In 1919 Lord Rutherford observed the first **nuclear transformation**, the change of one element into another. He found that by bombarding $^{14}_7\text{N}$ with α particles, the nuclide $^{17}_8\text{O}$ could be produced:



Fourteen years later, Irene Curie and her husband Frederick Joliot observed a similar transformation from aluminum to phosphorus



where ^1_0n represents a neutron.

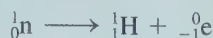
Over the years, many other nuclear transformations have been achieved, mostly using **particle accelerators**, which, as the name reveals, are devices used to give particles very high velocities. Because of the electrostatic repulsion between the

CHEMICAL IMPACT

Stellar Nucleosynthesis

How did all the matter around us originate? The scientific answer to this question is a theory called *stellar nucleosynthesis*, literally, the formation of nuclei in stars.

Many scientists believe that our universe originated as a cloud of neutrons that became unstable and produced an immense explosion, giving this model its name—the *big bang theory*. The model postulates that, following the initial explosion, neutrons decomposed into protons and electrons,



which eventually recombined to form clouds of hydrogen. Over the eons, gravitational forces caused many of these hydrogen clouds to contract and heat up sufficiently to reach temperatures where proton fusion was possible, which released large quantities of energy. When the tendency to expand due to the heat from fusion and the tendency to contract due to the forces of gravity are balanced, a stable young star such as our sun can be formed.

Eventually, when the supply of hydrogen is exhausted, the core of the star will again contract with further heating until temperatures are reached where fusion of helium nuclei can occur, leading to the formation of ${}_{6}^{12}\text{C}$ and ${}_{8}^{16}\text{O}$ nuclei. In turn, when the supply of helium nuclei runs out, further contraction and heating will occur, until fusion of heavier nuclei takes place. This process occurs repeatedly, forming heavier and heavier nuclei until iron nuclei are formed. Because the iron nucleus is the most stable of all, energy is required to fuse iron nuclei. This endothermic fusion process cannot furnish energy to sustain the star, and therefore it cools to a small, dense *white dwarf*.

The evolution just described is characteristic of small and medium-sized stars. Much larger stars, however, become unstable at some time during their evolution and undergo a *supernova explosion*. In this explosion, some medium-mass nuclei are fused to form heavy elements. Also, some light nuclei capture neutrons. These neutron-rich nuclei then pro-



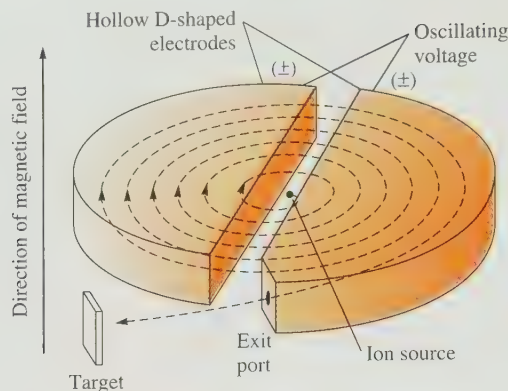
Image of a portion of the Cygnus Loop supernova remnant, taken by the Hubble space telescope.

duce β particles, increasing their atomic number with each event. This eventually leads to heavy nuclei. In fact, almost all nuclei heavier than iron are thought to originate from supernova explosions. The debris of a supernova explosion thus contains a large variety of elements and might eventually form a solar system such as our own.

Although other theories for the origin of matter have been suggested, there is much evidence to support the big bang theory, and it continues to be widely accepted.

For more information see V. E. Viola, "Formation of the chemical elements and the evolution of our universe," *J. Chem. Ed.* **67** (1990): 723.

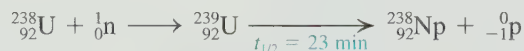
target nucleus and a positive ion, accelerators are needed when positive ions are used as bombarding particles. The particle, accelerated to a very high velocity, can overcome the repulsion and penetrate the target nucleus, thus effecting the transformation. A schematic diagram of one type of particle accelerator, the **cyclotron**, is shown in Fig. 18.5. The ion is introduced at the center of the cyclotron and is accelerated in an expanding spiral path by use of alternating electric fields in the presence of a magnetic field. The **linear accelerator** illustrated in Fig. 18.6 employs changing electric fields to achieve high velocities on a linear pathway.

**FIGURE 18.5**

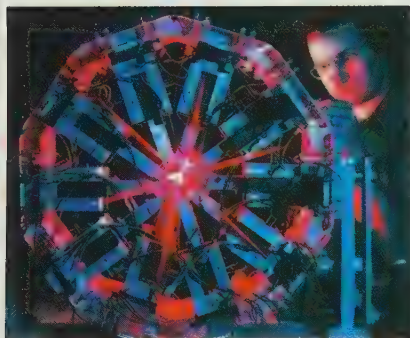
A schematic diagram of a cyclotron. The ion is introduced in the center and is pulled back and forth between the hollow D-shaped electrodes by constant reversals of the electric field. Magnets above and below these electrodes produce a spiral path that expands as the particle velocity increases. When the particle has sufficient speed, it exits the accelerator and is directed at the target nucleus.

In addition to positive ions, neutrons are often employed as bombarding particles to effect nuclear transformations. Because neutrons are uncharged and thus not repelled electrostatically by a target nucleus, they are readily absorbed by many nuclei, leading to new nuclides. The most common source of neutrons for this purpose is a fission reactor (see Section 18.6).

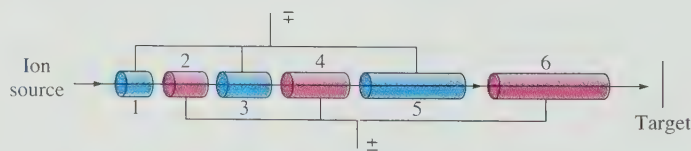
By using neutron and positive-ion bombardment, scientists have been able to extend the periodic table. Prior to 1940, the heaviest known element was uranium ($Z = 92$), but in 1940, neptunium ($Z = 93$) was produced by neutron bombardment of $^{238}_{92}\text{U}$. The process initially gives $^{239}_{92}\text{U}$, which decays to $^{239}_{93}\text{Np}$ by β -particle production:



In the years since 1940, the elements with atomic numbers 93 through 112, called the **transuranium elements**,* have been synthesized. Many of these elements



A physicist works with a small cyclotron at the University of California at Berkeley.

**FIGURE 18.6**

Schematic diagram of a linear accelerator, which uses a changing electric field to accelerate a positive ion along a linear path. As the ion leaves the source, the odd-numbered tubes are negatively charged, and the even-numbered tubes are positively charged. The positive ion is thus attracted into tube 1. As the ion leaves tube 1, the tube polarities are reversed. Now tube 1 is positive, repelling the positive ion, and tube 2 is negative, attracting the positive ion. This process continues, eventually producing high particle velocity.

*For more information, see G. B. Kauffman, "Beyond uranium," *Chem. Eng. News* (Nov. 19, 1990): 18.

TABLE 18.4 Syntheses of Some of the Transuranium Elements

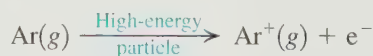
Element	Neutron Bombardment	Half-Life
Neptunium ($Z = 93$)	${}^{238}_{92}\text{U} + {}^1_0\text{n} \longrightarrow {}^{239}_{93}\text{Np} + {}^0_{-1}\text{e}$	2.35 days (${}^{239}_{93}\text{Np}$)
Plutonium ($Z = 94$)	${}^{239}_{93}\text{Np} \longrightarrow {}^{239}_{94}\text{Pu} + {}^0_{-1}\text{e}$	24,400 years (${}^{239}_{94}\text{Pu}$)
Americium ($Z = 95$)	${}^{239}_{94}\text{Pu} + 2 {}^1_0\text{n} \longrightarrow {}^{241}_{94}\text{Pu} \longrightarrow {}^{241}_{95}\text{Am} + {}^0_{-1}\text{e}$	458 years (${}^{241}_{95}\text{Am}$)
Element	Positive-Ion Bombardment	Half-Life
Curium ($Z = 96$)	${}^{239}_{94}\text{Pu} + {}^4_2\text{He} \longrightarrow {}^{242}_{96}\text{Cm} + {}^1_0\text{n}$	163 days (${}^{242}_{96}\text{Cm}$)
Californium ($Z = 98$)	${}^{242}_{96}\text{Cm} + {}^4_2\text{He} \longrightarrow {}^{245}_{98}\text{Cf} + {}^1_0\text{n}$ or ${}^{238}_{92}\text{U} + {}^{12}_6\text{C} \longrightarrow {}^{246}_{98}\text{Cf} + 4 {}^1_0\text{n}$	44 minutes (${}^{245}_{98}\text{Cf}$)
Rutherfordium ($Z = 104$)	${}^{249}_{98}\text{Cf} + {}^{12}_6\text{C} \longrightarrow {}^{257}_{104}\text{Rf} + 4 {}^1_0\text{n}$	
Dubnium ($Z = 105$)	${}^{249}_{98}\text{Cf} + {}^{15}_7\text{N} \longrightarrow {}^{260}_{105}\text{Db} + 4 {}^1_0\text{n}$	
Seaborgium ($Z = 106$)	${}^{249}_{98}\text{Cf} + {}^{18}_8\text{O} \longrightarrow {}^{263}_{106}\text{Sg} + 4 {}^1_0\text{n}$	

have very short half-lives, as shown in Table 18.4. As a result, only a few atoms of some have ever been formed. This of course makes the chemical characterization of these elements extremely difficult.

18.4 Detection and Uses of Radioactivity

Geiger counters are often called *survey meters* in industry.

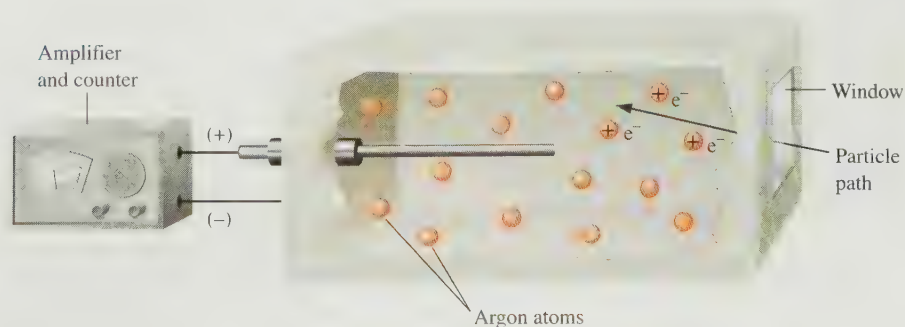
Although various instruments measure radioactivity levels, the most familiar of them is the **Geiger–Müller counter**, or **Geiger counter** (see Fig. 18.7). This instrument takes advantage of the fact that the high-energy particles from radioactive decay processes produce ions when they travel through matter. The probe of the Geiger counter is filled with argon gas, which can be ionized by a rapidly moving particle. This reaction is demonstrated by the equation:



Normally, a sample of argon gas will not conduct a current when an electrical potential is applied. However, the formation of ions and electrons produced by the

FIGURE 18.7

A schematic representation of a Geiger–Müller counter. The high-energy radioactive particle enters the window and ionizes argon atoms along its path. The resulting ions and electrons produce a momentary current pulse, which is amplified and counted.





Brigham Young researcher Scott Woodward taking a bone sample for carbon-14 dating at an archeological site in Egypt.

Radioactive nuclides are often called **radionuclides**. Carbon dating is based on the radionuclide $^{14}_6\text{C}$.

The $^{14}_6\text{C}/^{12}_6\text{C}$ ratio is the basis for carbon-14 dating.



A dendrochronologist cutting a section from a dead tree in South Africa.

passage of the high-energy particle allows a momentary current to flow. Electronic devices detect this current flow, and the number of these events can be counted. Thus the decay rate of the radioactive sample can be determined.

Another instrument often used to detect levels of radioactivity is a **scintillation counter**, which takes advantage of the fact that certain substances, such as zinc sulfide, give off light when they are struck by high-energy radiation. A photocell senses the flashes of light that occur as the radiation strikes and thus measures the number of decay events per unit of time.

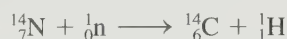
Dating by Radioactivity

Archeologists, geologists, and others involved in reconstructing the ancient history of the earth rely heavily on radioactivity to provide accurate dates for artifacts and rocks. A method that has been very important for dating ancient articles made from wood or cloth is **radiocarbon dating**, or **carbon-14 dating**, a technique originated in the 1940s by Willard Libby, an American chemist who received a Nobel Prize for his efforts in this field.

Radiocarbon dating is based on the radioactivity of the nuclide $^{14}_6\text{C}$, which decays via β -particle production:



Carbon-14 is continuously produced in the atmosphere when high-energy neutrons from space collide with nitrogen-14:



Thus carbon-14 is continuously produced by this process, and it continuously decomposes through β -particle production. Over the years, the rates for these two processes have become equal, and like a participant in a chemical reaction at equilibrium, the amount of $^{14}_6\text{C}$ that is present in the atmosphere remains approximately constant.

Carbon-14 can be used to date wood and cloth artifacts because the $^{14}_6\text{C}$, along with the other carbon isotopes in the atmosphere, reacts with oxygen to form carbon dioxide. A living plant consumes carbon dioxide in the photosynthesis process and incorporates the carbon, including $^{14}_6\text{C}$, into its molecules. As long as the plant lives, the $^{14}_6\text{C}/^{12}_6\text{C}$ ratio in its molecules remains the same as in the atmosphere because of the continuous uptake of carbon. However, as soon as a tree is cut to make a wooden bowl or a flax plant is harvested to make linen, the $^{14}_6\text{C}/^{12}_6\text{C}$ ratio begins to decrease because of the radioactive decay of $^{14}_6\text{C}$ (the $^{12}_6\text{C}$ nuclide is stable). Since the half-life of $^{14}_6\text{C}$ is 5730 years, a wooden bowl found in an archeological dig showing a $^{14}_6\text{C}/^{12}_6\text{C}$ ratio that is half that found in currently living trees is approximately 5730 years old. This reasoning assumes that the current $^{14}_6\text{C}/^{12}_6\text{C}$ ratio is the same as that found in ancient times.

Dendrochronologists, scientists who date trees from annual growth rings, have used data collected from long-lived species of trees, such as bristlecone pines and sequoias, to show that the $^{14}_6\text{C}$ content of the atmosphere has changed significantly over the ages. These data have been used to derive correction factors that allow very accurate dates to be determined from the observed $^{14}_6\text{C}/^{12}_6\text{C}$ ratio in an artifact, especially for artifacts 10,000 years old or younger. Recent measurements of uranium/thorium ratios in ancient coral indicate that dates in the 20,000- to 30,000-year range may have errors as large as 3000 years. As a result, efforts are now being made to recalibrate the $^{14}_6\text{C}$ dates over this period.

SAMPLE EXERCISE 18.5

¹⁴C Dating

The remnants of an ancient fire in a cave in Africa showed a ¹⁴C decay rate of 3.1 counts per minute per gram of carbon. Assuming that the decay rate of ¹⁴C in freshly cut wood (corrected for changes in the ¹⁴C content of the atmosphere) is 13.6 counts per minute per gram of carbon, calculate the age of the remnants. The half-life of ¹⁴C is 5730 years.

SOLUTION

The key to solving this problem is to realize that the decay rates given are directly proportional to the number of ¹⁴C nuclides present. Radioactive decay follows first-order kinetics:

$$\text{Rate} = kN$$

Thus

$$\begin{aligned} \frac{3.1 \text{ counts/min} \cdot \text{g}}{13.6 \text{ counts/min} \cdot \text{g}} &= \frac{\text{rate at time } t}{\text{rate at time 0}} = \frac{kN}{kN_0} \\ &= \frac{N}{N_0} = 0.23 \end{aligned}$$

Number of nuclides
 present at time t
 Number of nuclides
 present at time 0

We can now use the integrated first-order rate law:

$$\ln\left(\frac{N}{N_0}\right) = -kt$$

where $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{5730 \text{ years}}$

to solve for t , the time elapsed since the campfire:

$$\ln\left(\frac{N}{N_0}\right) = \ln(0.23) = -\left(\frac{0.693}{5730 \text{ years}}\right)t$$

Solving this equation gives $t = 12,000$ years; the campfire in the cave occurred about 12,000 years ago.

See Exercises 18.27 and 18.28.

One drawback of radiocarbon dating is that a fairly large piece of the object (from a half to several grams) must be burned to form carbon dioxide, which is then analyzed for radioactivity. Another method for counting ¹⁴C nuclides avoids destruction of a significant portion of a valuable artifact. This technique, requiring only about 10⁻³ g, uses a mass spectrometer (see Chapter 3), in which the carbon atoms are ionized and accelerated through a magnetic field that deflects their path. Because of their different masses, the various ions are deflected by different amounts and can be counted separately. This allows a very accurate determination of the ¹⁴C/¹²C ratio in the sample.

In their attempts to establish the geologic history of the earth, geologists have made extensive use of radioactivity. For example, since ²³⁸U decays to the stable

$^{206}_{82}\text{Pb}$ nuclide, the ratio of $^{206}_{82}\text{Pb}$ to $^{238}_{92}\text{U}$ in a rock can, under favorable circumstances, be used to estimate the age of the rock. The radioactive nuclide $^{176}_{71}\text{Lu}$, which decays to $^{176}_{72}\text{Hf}$, has a half-life of 37 billion years (only 186 nuclides out of 10 trillion decay each year!). Thus this nuclide can be used to date very old rocks. With this technique, scientists have estimated that the earth's crust formed 4.3 billion years ago.

SAMPLE EXERCISE 18.6

Because the half-life of $^{238}_{92}\text{U}$ is very long compared with those of the other members of the decay series (see Table 18.3) to reach $^{206}_{82}\text{Pb}$, the number of nuclides present in intermediate stages of decay is negligible. That is, once a $^{238}_{92}\text{U}$ nuclide starts to decay, it reaches $^{206}_{82}\text{Pb}$ relatively fast.

Dating by Radioactivity

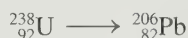
A rock containing $^{238}_{92}\text{U}$ and $^{206}_{82}\text{Pb}$ was examined to determine its approximate age. Analysis showed the ratio of $^{206}_{82}\text{Pb}$ atoms to $^{238}_{92}\text{U}$ atoms to be 0.115. Assuming that no lead was originally present, that all the $^{206}_{82}\text{Pb}$ formed over the years has remained in the rock, and that the number of nuclides in intermediate stages of decay between $^{238}_{92}\text{U}$ and $^{206}_{82}\text{Pb}$ is negligible, calculate the age of the rock. The half-life of $^{238}_{92}\text{U}$ is 4.5×10^9 years.

SOLUTION

This problem can be solved using the integrated first-order rate law:

$$\ln\left(\frac{N}{N_0}\right) = -kt = -\left(\frac{0.693}{4.5 \times 10^9 \text{ years}}\right)t$$

where N/N_0 represents the ratio of $^{238}_{92}\text{U}$ atoms now found in the rock to the number present when the rock was formed. We are assuming that each $^{206}_{82}\text{Pb}$ nuclide present must have come from decay of a $^{238}_{92}\text{U}$:



Thus

Number of $^{238}_{92}\text{U}$ atoms originally present	=	number of $^{206}_{82}\text{Pb}$ atoms now present	+	number of $^{238}_{92}\text{U}$ atoms now present
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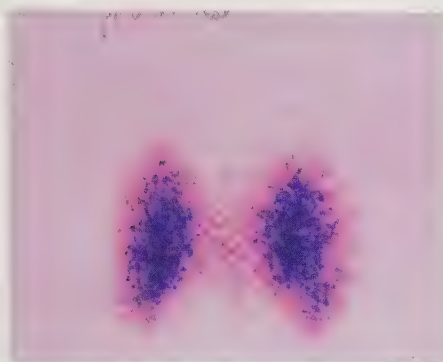
$$\frac{\text{Atoms of } ^{206}_{82}\text{Pb} \text{ now present}}{\text{Atoms of } ^{238}_{92}\text{U} \text{ now present}} = 0.115 = \frac{0.115}{1.000} = \frac{115}{1000}$$

Think carefully about what this means. For every 1115 $^{238}_{92}\text{U}$ atoms originally present in the rock, 115 have been changed to $^{206}_{82}\text{Pb}$ and 1000 remain as $^{238}_{92}\text{U}$. Thus

$$\begin{aligned} \frac{N}{N_0} &= \frac{\overset{\text{Now present}}{^{238}_{92}\text{U}}}{\underbrace{^{206}_{82}\text{Pb} + ^{238}_{92}\text{U}}_{\text{^{238}_{92}\text{U} originally present}}} = \frac{1000}{1115} = 0.8969 \\ \ln\left(\frac{N}{N_0}\right) &= \ln(0.8969) = -\left(\frac{0.693}{4.5 \times 10^9 \text{ years}}\right)t \\ t &= 7.1 \times 10^8 \text{ years} \end{aligned}$$

This is the approximate age of the rock. It was formed sometime in the Cambrian period.

See Exercises 18.29 and 18.30.

**FIGURE 18.8**

After consumption of Na^{131}I , the patient's thyroid is scanned for radioactivity levels to determine the efficiency of iodine absorption. (left) A normal thyroid. (right) An enlarged thyroid.

A pellet containing radioactive ^{131}I .

Medical Applications of Radioactivity

Although the rapid advances of the medical sciences in recent decades are due to many causes, one of the most important has been the discovery and use of **radio-tracers**, radioactive nuclides that can be introduced into organisms in food or drugs and whose pathways can be *traced* by monitoring their radioactivity. For example, the incorporation of nuclides such as ^{14}C and ^{32}P into nutrients has produced important information about metabolic pathways.

Iodine-131 has proved very useful in the diagnosis and treatment of illnesses of the thyroid gland. Patients drink a solution containing small amounts of Na^{131}I , and the uptake of the iodine by the thyroid gland is monitored with a scanner (see Fig. 18.8).

Thallium-201 can be used to assess the damage to the heart muscle in a person who has suffered a heart attack, because thallium is concentrated in healthy muscle tissue. Technetium-99m is also taken up by normal heart tissue and is used for damage assessment in a similar way.

Radiotracers provide sensitive and noninvasive methods for learning about biologic systems, for detection of disease, for monitoring the action and effectiveness of drugs, and for early detection of pregnancy, and their usefulness should continue to grow. Some useful radiotracers are listed in Table 18.5.

TABLE 18.5 Some Radioactive Nuclides, with Half-Lives and Medical Applications as Radiotracers

Nuclide	Half-Life	Area of the Body Studied
^{131}I	8.1 days	Thyroid
^{59}Fe	45.1 days	Red blood cells
^{99}Mo	67 hours	Metabolism
^{32}P	14.3 days	Eyes, liver, tumors
^{51}Cr	27.8 days	Red blood cells
^{87}Sr	2.8 hours	Bones
$^{99\text{m}}\text{Tc}$	6.0 hours	Heart, bones, liver, and lungs
^{133}Xe	5.3 days	Lungs
^{24}Na	14.8 hours	Circulatory system

18.5 Thermodynamic Stability of the Nucleus

We can determine the thermodynamic stability of a nucleus by calculating the change in potential energy that would occur if that nucleus were formed from its constituent protons and neutrons. For example, let's consider the hypothetical process of forming a $^{16}_8\text{O}$ nucleus from eight neutrons and eight protons:



The energy change associated with this process can be calculated by comparing the sum of the masses of eight protons and eight neutrons with that of the oxygen nucleus:

$$\begin{aligned}\text{Mass of } (8\text{}^1_0\text{n} + 8\text{}^1_1\text{H}) &= 8(1.67493 \times 10^{-24} \text{ g}) + 8(1.67262 \times 10^{-24} \text{ g}) \\ &\quad \begin{array}{c} \uparrow \\ \text{Mass of } ^1_0\text{n} \end{array} \quad \begin{array}{c} \uparrow \\ \text{Mass of } ^1_1\text{H} \end{array} \\ &= 2.67804 \times 10^{-23} \text{ g} \\ \text{Mass of } ^{16}_8\text{O nucleus} &= 2.65535 \times 10^{-23} \text{ g}\end{aligned}$$

The difference in mass for one nucleus is

$$\text{Mass of } ^{16}_8\text{O} - \text{mass of } (8\text{}^1_0\text{n} + 8\text{}^1_1\text{H}) = -2.269 \times 10^{-25} \text{ g}$$

The difference in mass for formation of 1 mole of $^{16}_8\text{O}$ nuclei is therefore

$$(-2.269 \times 10^{-25} \text{ g/nucleus})(6.022 \times 10^{23} \text{ nuclei/mol}) = -0.1366 \text{ g/mol}$$

Thus 0.1366 g of mass would be lost if 1 mole of oxygen-16 were formed from protons and neutrons. What is the reason for this difference in mass, and how can this information be used to calculate the energy change that accompanies this process?

The answers to these questions can be found in the work of Albert Einstein. As we discussed in Section 7.2, Einstein's theory of relativity showed that energy should be considered a form of matter. His famous equation

$$E = mc^2$$

where c is the speed of light, gives the relationship between a quantity of energy and its mass. When a system gains or loses energy, it also gains or loses a quantity of mass, given by E/c^2 . Thus the mass of a nucleus is less than that of its component nucleons because the process is so exothermic.

Einstein's equation in the form

$$\text{Energy change} = \Delta E = \Delta mc^2$$

where Δm is the change in mass, or the **mass defect**, can be used to calculate ΔE for the hypothetical formation of a nucleus from its component nucleons.

Energy is a form of matter.

The energy changes associated with normal chemical reactions are small enough that the corresponding mass changes are not detectable.

SAMPLE EXERCISE 18.7

Nuclear Binding Energy I

Calculate the change in energy if 1 mol $^{16}_8\text{O}$ nuclei was formed from neutrons and protons.

SOLUTION

We have already calculated that 0.1366 g of mass would be lost in the hypothetical process of assembling 1 mol $^{16}_8\text{O}$ nuclei from the component nucleons. We can calculate the change in energy for this process from

$$\Delta E = \Delta mc^2$$

where

$$c = 3.00 \times 10^8 \text{ m/s} \quad \text{and} \quad \Delta m = -0.1366 \text{ g/mol} = -1.366 \times 10^{-4} \text{ kg/mol}$$

Thus

$$\Delta E = (-1.366 \times 10^{-4} \text{ kg/mol})(3.00 \times 10^8 \text{ m/s})^2 = -1.23 \times 10^{13} \text{ J/mol}$$

The negative sign for the ΔE value indicates that the process is exothermic. Energy, and thus mass, is lost from the system.

See Exercises 18.31 through 18.33.

The energy changes observed for nuclear processes are extremely large compared with those observed for chemical and physical changes. Thus nuclear processes constitute a potentially valuable energy resource.

The thermodynamic stability of a particular nucleus is normally represented as energy released per nucleon. To illustrate how this quantity is obtained, we will continue to consider $^{16}_8\text{O}$. First, we calculate ΔE per nucleus by dividing the molar value from Sample Exercise 18.7 by Avogadro's number:

$$\Delta E \text{ per } ^{16}_8\text{O nucleus} = \frac{-1.23 \times 10^{13} \text{ J/mol}}{6.022 \times 10^{23} \text{ nuclei/mol}} = -2.04 \times 10^{-11} \text{ J/nucleus}$$

In terms of a more convenient energy unit, a million electronvolts (MeV), where

$$1 \text{ MeV} = 1.60 \times 10^{-13} \text{ J}$$

$$\begin{aligned} \Delta E \text{ per } ^{16}_8\text{O nucleus} &= (-2.04 \times 10^{-11} \text{ J/nucleus}) \left(\frac{1 \text{ MeV}}{1.60 \times 10^{-13} \text{ J}} \right) \\ &= -1.28 \times 10^2 \text{ MeV/nucleus} \end{aligned}$$

Next, we can calculate the value of ΔE per nucleon by dividing by A , the sum of neutrons and protons:

$$\begin{aligned} \Delta E \text{ per nucleon for } ^{16}_8\text{O} &= \frac{-1.28 \times 10^2 \text{ MeV/nucleus}}{16 \text{ nucleons/nucleus}} \\ &= -7.98 \text{ MeV/nucleon} \end{aligned}$$

This means that 7.98 MeV of energy per nucleon would be *released* if $^{16}_8\text{O}$ were formed from neutrons and protons. The energy required to *decompose* this nucleus into its components has the same numeric value but with a positive sign (since energy is required). This is called the **binding energy** per nucleon for $^{16}_8\text{O}$.

The values of the binding energy per nucleon for the various nuclides are shown in Fig. 18.9. Note that the most stable nuclei (those requiring the largest energy per nucleon to decompose the nucleus) occur at the top of the curve. The most stable nucleus known is $^{56}_{26}\text{Fe}$, which has a binding energy per nucleon of 8.79 MeV.

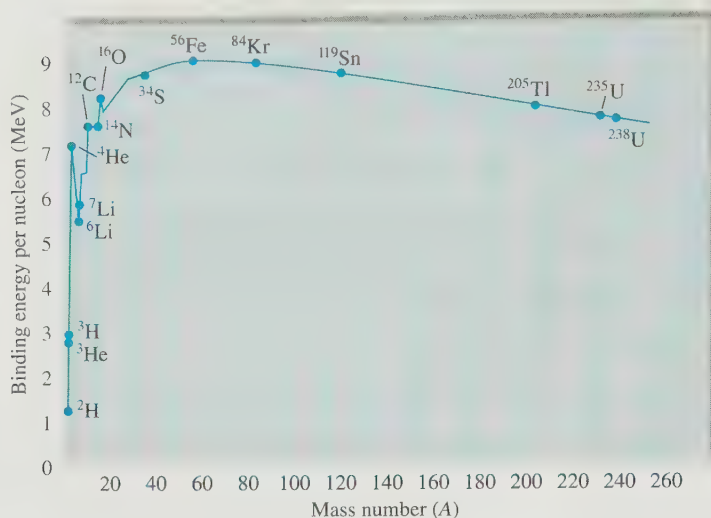
SAMPLE EXERCISE 18.8

Nuclear Binding Energy II

Calculate the binding energy per nucleon for the ^4_2He nucleus (atomic masses: $^4_2\text{He} = 4.0026 \text{ amu}$; $^1_1\text{H} = 1.0078 \text{ amu}$).

SOLUTION

First, we must calculate the mass defect (Δm) for ^4_2He . Since atomic masses (which include the electrons) are given, we must decide how to account for the electron mass:

**FIGURE 18.9**

The binding energy per nucleon as a function of mass number. The most stable nuclei are at the top of the curve. The most stable nucleus is $^{56}_{26}\text{Fe}$.

Since atomic masses include the masses of the electrons, to obtain the mass of a given atomic nucleus from its atomic mass, we must subtract the mass of the electrons.

$$4.0026 = \text{mass of } {}^4_2\text{He atom} = \text{mass of } {}^4_2\text{He nucleus} + 2m_e$$

Electron mass

$$1.0078 = \text{mass of } {}^1_1\text{H atom} = \text{mass of } {}^1_1\text{H nucleus} + m_e$$

Thus, since a ${}^4_2\text{He}$ nucleus is “synthesized” from two protons and two neutrons, we see that

$$\begin{aligned} \Delta m &= \underbrace{(4.0026 - 2m_e)}_{\substack{\text{Mass of } {}^4_2\text{He} \\ \text{nucleus}}} - \left[\underbrace{2(1.0078 - m_e)}_{\substack{\text{Mass of } {}^1_1\text{H} \\ \text{nucleus (proton)}}} + \underbrace{2(1.0087)}_{\substack{\text{Mass of} \\ \text{neutron}}} \right] \\ &= 4.0026 - 2m_e - 2(1.0078) + 2m_e - 2(1.0087) \\ &= 4.0026 - 2(1.0078) - 2(1.0087) \\ &= -0.0304 \text{ amu} \end{aligned}$$

Note that in this case the electron mass cancels out in taking the difference. This will always happen in this type of calculation if the atomic masses are used both for the nuclide of interest and for ${}^1_1\text{H}$. Thus 0.0304 amu of mass is *lost* per ${}^4_2\text{He}$ nucleus formed.

The corresponding energy change can be calculated from

$$\Delta E = \Delta mc^2$$

where

$$\begin{aligned} \Delta m &= -0.0304 \frac{\text{amu}}{\text{nucleus}} = \left(-0.0304 \frac{\text{amu}}{\text{nucleus}} \right) \left(1.66 \times 10^{-27} \frac{\text{kg}}{\text{amu}} \right) \\ &= -5.04 \times 10^{-29} \frac{\text{kg}}{\text{nucleus}} \end{aligned}$$

and

$$c = 3.00 \times 10^8 \text{ m/s}$$

$$\begin{aligned} \text{Thus } \Delta E &= \left(-5.04 \times 10^{-29} \frac{\text{kg}}{\text{nucleus}} \right) \left(3.00 \times 10^8 \frac{\text{m}}{\text{s}} \right)^2 \\ &= -4.54 \times 10^{-12} \text{ J/nucleus} \end{aligned}$$

This means that 4.54×10^{-12} J of energy is *released* per nucleus formed and that 4.54×10^{-12} J would be required to decompose the nucleus into the constituent neutrons and protons. Thus the binding energy (BE) per nucleon is

$$\begin{aligned}\text{BE per nucleon} &= \frac{4.54 \times 10^{-12} \text{ J/nucleus}}{4 \text{ nucleons/nucleus}} \\ &= 1.14 \times 10^{-12} \text{ J/nucleon} \\ &= \left(1.14 \times 10^{-12} \frac{\text{J}}{\text{nucleon}} \right) \left(\frac{1 \text{ MeV}}{1.60 \times 10^{-13} \text{ J}} \right) \\ &= 7.13 \text{ MeV/nucleon}\end{aligned}$$

See Exercises 18.34 through 18.36.

18.6 Nuclear Fission and Nuclear Fusion

The graph shown in Fig. 18.9 has very important implications for the use of nuclear processes as sources of energy. Recall that energy is released, that is, ΔE is negative, when a process goes from a less stable to a more stable state. The higher a nuclide is on the curve, the more stable it is. This means that two types of nuclear processes will be exothermic (see Fig. 18.10):

1. Combining two light nuclei to form a heavier, more stable nucleus. This process is called **fusion**.
2. Splitting a heavy nucleus into two nuclei with smaller mass numbers. This process is called **fission**.

Because of the large binding energies involved in holding the nucleus together, both these processes involve energy changes more than a million times larger than those associated with chemical reactions.

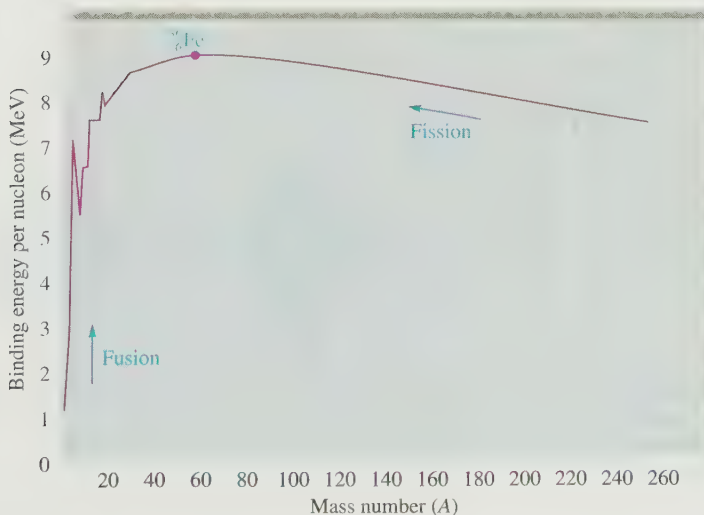


FIGURE 18.10
Both fission and fusion produce more stable nuclides and are thus exothermic.

Nuclear Fission

Nuclear fission was discovered in the late 1930s when $^{235}_{92}\text{U}$ nuclides bombarded with neutrons were observed to split into two lighter elements:



This process, shown schematically in Fig. 18.11, releases 3.5×10^{-11} J of energy per event, which translates to 2.1×10^{13} J per mole of $^{235}_{92}\text{U}$. Compare this figure with that for the combustion of methane, which releases only 8.0×10^5 J of energy per mole. The fission of $^{235}_{92}\text{U}$ produces about 26 million times more energy than the combustion of methane.

The process shown in Fig. 18.11 is only one of the many fission reactions that $^{235}_{92}\text{U}$ can undergo. Another is



In fact, over 200 different isotopes of 35 different elements have been observed among the fission products of $^{235}_{92}\text{U}$.

In addition to the product nuclides, neutrons are also produced in the fission reactions of $^{235}_{92}\text{U}$. This makes it possible to have a self-sustaining fission process—a **chain reaction** (see Fig. 18.12). For the fission process to be self-sustaining, at least one neutron from each fission event must go on to split another nucleus. If, on average, *less than one* neutron causes another fission event, the process dies out and the reaction is said to be **subcritical**. If *exactly one* neutron from each fission event causes another fission event, the process sustains itself at the same level and is said to be **critical**. If *more than one* neutron from each fission event causes another fission event, the process rapidly escalates and the heat buildup causes a violent explosion. This situation is described as **supercritical**.

To achieve the critical state, a certain mass of fissionable material, called the **critical mass**, is needed. If the sample is too small, too many neutrons escape before they have a chance to cause a fission event, and the process stops. This is illustrated in Fig. 18.13.

During World War II, an intense research effort called the Manhattan Project was carried out by the United States to build a bomb based on the principles of nuclear fission. This program produced the fission bombs that were used with devas-

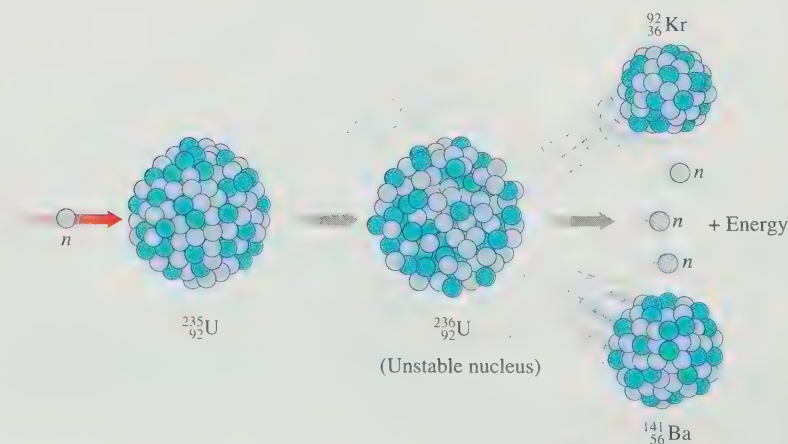
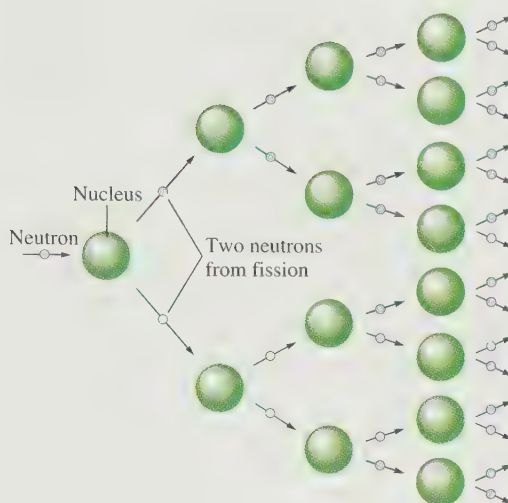


FIGURE 18.11

On capturing a neutron, the $^{235}_{92}\text{U}$ nucleus undergoes fission to produce two lighter nuclides, free neutrons (typically three), and a large amount of energy.

**FIGURE 18.12**

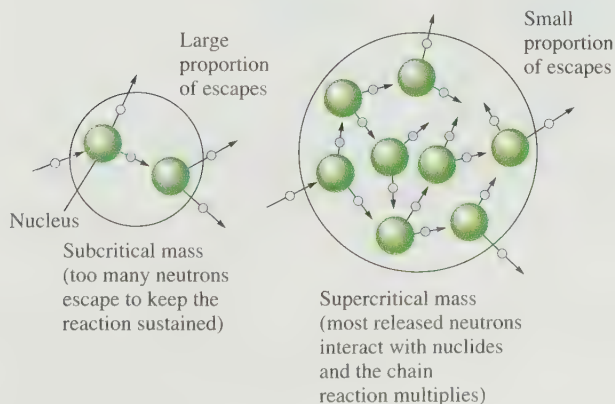
Representation of a fission process in which each event produces two neutrons, which can go on to split other nuclei, leading to a self-sustaining chain reaction.

tating effects on the cities of Hiroshima and Nagasaki in 1945. Basically, a fission bomb operates by suddenly combining subcritical masses of fissionable material to form a supercritical mass, thereby producing an explosion of incredible intensity.

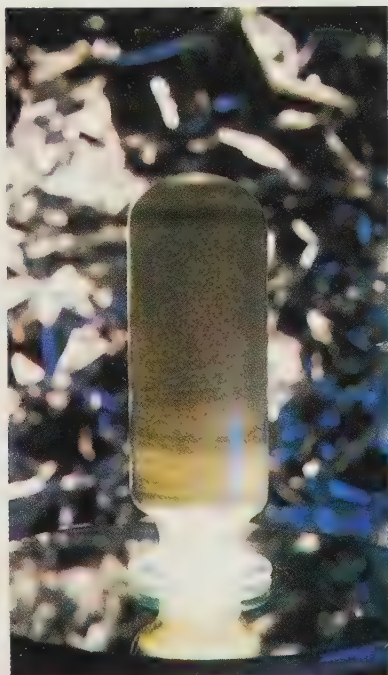
Nuclear Reactors

Because of the tremendous energies involved, it seemed desirable to develop the fission process as an energy source to produce electricity. To accomplish this, reactors were designed in which controlled fission can occur. The resulting energy is used to heat water to produce steam to run turbine generators, in much the same way that a coal-burning power plant generates energy. A schematic diagram of a nuclear power plant is shown in Fig. 18.14.

In the **reactor core**, shown in Fig. 18.15, uranium that has been enriched to approximately 3% $^{235}_{92}\text{U}$ (natural uranium contains only 0.7% $^{235}_{92}\text{U}$) is housed in cylinders. A **moderator** surrounds the cylinders to slow down the neutrons so that the uranium fuel can capture them more efficiently. **Control rods**, composed of substances that absorb neutrons, are used to regulate the power level of the reactor. The reactor is designed so that should a malfunction occur, the control

**FIGURE 18.13**

If the mass of fissionable material is too small, most of the neutrons escape before causing another fission event, and the process dies out.



Uranium oxide (refined uranium).

rods are automatically inserted into the core to stop the reaction. A liquid (usually water) is circulated through the core to extract the heat generated by the energy of fission; the energy can then be passed on via a heat exchanger to water in the turbine system.

Although the concentration of $^{235}_{92}\text{U}$ in the fuel elements is not great enough to allow a supercritical mass to develop in the core, a failure of the cooling system can lead to temperatures high enough to melt the core. As a result, the building housing the core must be designed to contain the core even if meltdown occurs. A great deal of controversy now exists about the efficiency of the safety systems in nuclear power plants. Accidents such as the one at the Three Mile Island facility in Pennsylvania in 1979 and in Chernobyl,* Ukraine, in 1986 have led to questions about the wisdom of continuing to build fission-based power plants.

Breeder Reactors

One potential problem facing the nuclear power industry is the supply of $^{235}_{92}\text{U}$. Some scientists have suggested that we have nearly depleted those uranium deposits rich enough in $^{235}_{92}\text{U}$ to make production of fissionable fuel economically feasible. Because of this possibility, **breeder reactors** have been developed, in which fissionable fuel is actually produced while the reactor runs. In the breeder reactors now being

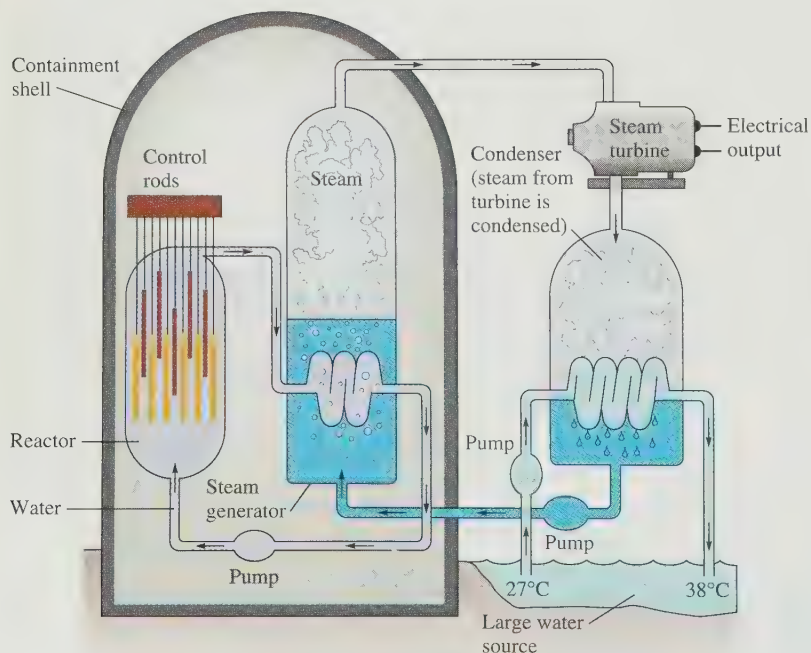


FIGURE 18.14

A schematic diagram of a nuclear power plant.

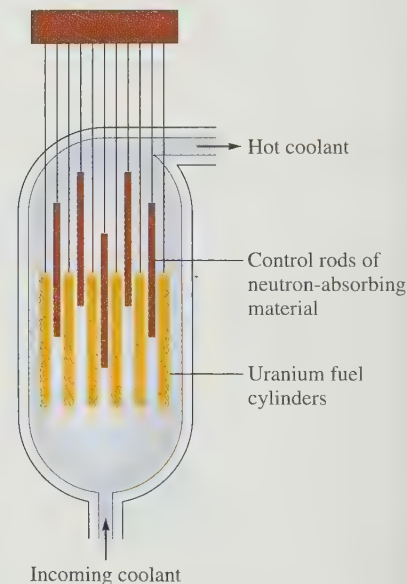
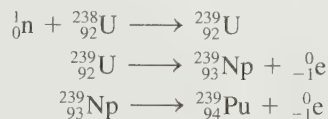


FIGURE 18.15

A schematic of a reactor core. The position of the control rods determines the level of energy production by regulating the amount of fission taking place.

*See C. A. Atwood, "Chernobyl—What happened?" *J. Chem. Ed.* **65** (1988): 1037.

studied, the major component of natural uranium, nonfissionable $^{238}_{92}\text{U}$, is changed to fissionable $^{239}_{94}\text{Pu}$. The reaction involves absorption of a neutron, followed by production of two β particles:

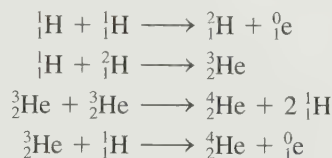


As the reactor runs and $^{235}_{92}\text{U}$ is split, some of the excess neutrons are absorbed by $^{238}_{92}\text{U}$ to produce $^{239}_{94}\text{Pu}$. The $^{239}_{94}\text{Pu}$ is then separated out and used to fuel another reactor. Such a reactor thus “breeds” nuclear fuel as it operates.

Although breeder reactors are now used in France, the United States is proceeding slowly with their development because of their controversial nature. One problem involves the hazards in handling plutonium, which flames on contact with air and is very toxic.

Fusion

Large quantities of energy are also produced by the fusion of two light nuclei. In fact, stars produce their energy through nuclear fusion. Our sun, which presently consists of 73% hydrogen, 26% helium, and 1% other elements, gives off vast quantities of energy from the fusion of protons to form helium:



Intense research is under way to develop a feasible fusion process because of the ready availability of many light nuclides (deuterium, ^2_1H , in seawater, for example) that can serve as fuel in fusion reactors. The major stumbling block is that high temperatures are required to initiate fusion. The forces that bind nucleons together to form a nucleus are effective only at *very small* distances ($\sim 10^{-13}$ cm). Thus, for two protons to bind together and thereby release energy, they must get very close together. But protons, because they are identically charged, repel each other electrostatically. This means that to get two protons (or two deuterons) close enough to bind together (the nuclear binding force is *not* electrostatic), they must be “shot” at each other at speeds high enough to overcome the electrostatic repulsion.

The electrostatic repulsion forces between two ^2_1H nuclei are so great that a temperature of 4×10^7 K is required to give them velocities large enough to cause them to collide with sufficient energy that the nuclear forces can bind the particles together and thus release the binding energy. This situation is represented in Fig. 18.16.

Currently, scientists are studying two types of systems to produce the extremely high temperatures required: high-powered lasers and heating by electric currents. At present, many technical problems remain to be solved, and it is not clear which method will prove more useful or when fusion might become a practical energy source. However, there is still hope that fusion will be a major energy source sometime in the future.

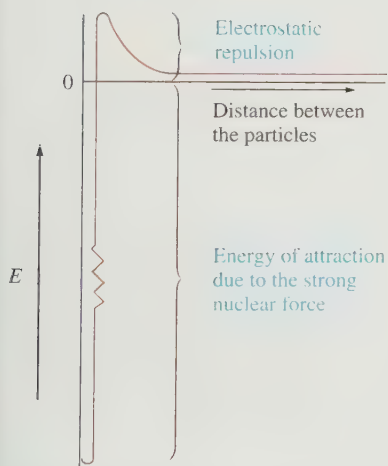


FIGURE 18.16

A plot of energy versus the separation distance for two ^2_1H nuclei. The nuclei must have sufficient velocities to get over the electrostatic repulsion “hill” and get close enough for the nuclear binding forces to become effective, thus “fusing” the particles into a new nucleus and releasing large quantities of energy. The binding force is at least 100 times the electrostatic repulsion.

18.7 Effects of Radiation

The ozone layer is discussed in Section 20.5.

Everyone knows that being hit by a train is very serious. The problem is the energy transfer involved. In fact, any source of energy is potentially harmful to organisms. Energy transferred to cells can break chemical bonds and cause malfunctioning of the cell systems. This fact is behind the concern about the ozone layer in the earth's upper atmosphere, which screens out high-energy ultraviolet radiation from the sun. Radioactive elements, which are sources of high-energy particles, are also potentially hazardous, although the effects are usually quite subtle. The reason for the subtlety of radiation damage is that even though high-energy particles are involved, the quantity of energy actually deposited in tissues *per event* is quite small. However, the resulting damage is no less real, although the effects may not be apparent for years.

Radiation damage to organisms can be classified as somatic or genetic damage. **Somatic damage** is damage to the organism itself, resulting in sickness or death. The effects may appear almost immediately if a massive dose of radiation is received; for smaller doses, damage may appear years later, usually in the form of cancer. **Genetic damage** is damage to the genetic machinery, which produces malfunctions in the offspring of the organism.

The biologic effects of a particular source of radiation depend on several factors:

1. *The energy of the radiation.* The higher the energy content of the radiation, the more damage it can cause. Radiation doses are measured in **rads** (which is short for *radiation absorbed dose*), where 1 rad corresponds to 10^{-2} J of energy deposited per kilogram of tissue.
2. *The penetrating ability of the radiation.* The particles and rays produced in radioactive processes vary in their abilities to penetrate human tissue: γ rays are highly penetrating, β particles can penetrate approximately 1 cm, and α particles are stopped by the skin.
3. *The ionizing ability of the radiation.* Extraction of electrons from biomolecules to form ions is particularly detrimental to their functions. The ionizing ability of radiation varies dramatically. For example, γ rays penetrate very deeply but cause only occasional ionization. On the other hand, α particles, although not very penetrating, are very effective at causing ionization and produce a dense trail of damage. Thus ingestion of an α -particle producer, such as plutonium, is particularly damaging.
4. *The chemical properties of the radiation source.* When a radioactive nuclide is ingested into the body, its effectiveness in causing damage depends on its residence time. For example, $^{85}_{36}\text{Kr}$ and $^{90}_{38}\text{Sr}$ are both β -particle producers. However, since krypton is chemically inert, it passes through the body quickly and does not have much time to do damage. Strontium, being chemically similar to calcium, can collect in bones, where it may cause leukemia and bone cancer.

Because of the differences in the behavior of the particles and rays produced by radioactive decay, both the energy dose of the radiation and its effectiveness in causing biologic damage must be taken into account. The **rem** (which is short for *roentgen equivalent for man*) is defined as follows:

$$\text{Number of rems} = (\text{number of rads}) \times \text{RBE}$$

TABLE 18.6 Effects of Short-Term Exposures to Radiation

Dose (rem)	Clinical Effect
0–25	Nondetectable
25–50	Temporary decrease in white blood cell counts
100–200	Strong decrease in white blood cell counts
500	Death of half the exposed population within 30 days after exposure

TABLE 18.7
Typical Radiation Exposures
for a Person Living in the
United States (1 millirem =
 10^{-3} rem)

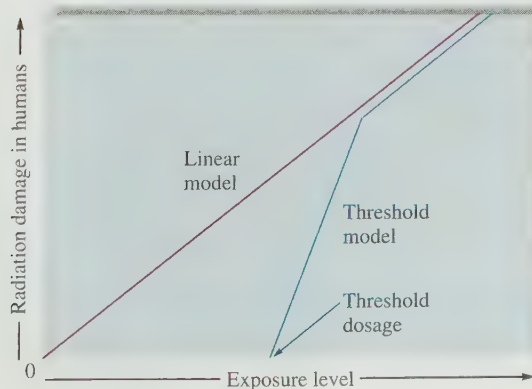
	Exposure (millirems/year)
Cosmic radiation	50
From the earth	47
From building materials	3
In human tissues	21
Inhalation of air	5
<i>Total from natural sources</i>	126
X-ray diagnosis	50
Radiotherapy	10
Internal diagnosis/ therapy	1
Nuclear power industry	0.2
TV tubes, industrial wastes, etc.	2
Radioactive fallout	4
<i>Total from human activities</i>	67
<i>Total</i>	193

where RBE represents the relative effectiveness of the radiation in causing biologic damage.

Table 18.6 shows the physical effects of short-term exposure to various doses of radiation, and Table 18.7 gives the sources and amounts of radiation exposure for a typical person in the United States. Note that natural sources contribute about twice as much as human activities to the total exposure. However, although the nuclear industry contributes only a small percentage of the total exposure, the major controversy associated with nuclear power plants is the *potential* for radiation hazards. These arise mainly from two sources: accidents allowing the release of radioactive materials and improper disposal of the radioactive products in spent fuel elements. The radioactive products of the fission of $^{235}_{92}\text{U}$, although only a small percentage of the total products, have half-lives of several hundred years and remain dangerous for a long time. Various schemes have been advanced for the disposal of these wastes. The one that seems to hold the most promise is the incorporation of the wastes into ceramic blocks and the burial of these blocks in geologically stable formations. At present, however, no disposal method has been accepted, and nuclear wastes continue to accumulate in temporary storage facilities.

Even if a satisfactory method for permanent disposal of nuclear wastes is found, there will continue to be concern about the effects of exposure to low levels of radiation. Exposure is inevitable from natural sources such as cosmic rays and radioactive minerals, and many people are also exposed to low levels of radiation from reactors, radioactive tracers, or diagnostic X rays. Currently, we have little reliable information on the long-term effects of low-level exposure to radiation.

Two models of radiation damage, illustrated in Fig. 18.17, have been proposed: the *linear model* and the *threshold model*. The linear model postulates that

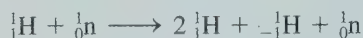
**FIGURE 18.17**

The two models for radiation damage. In the linear model, even a small dosage causes a proportional risk. In the threshold model, risk begins only after a certain dosage.

CHEMICAL IMPACT

Nuclear Physics: An Introduction

Nuclear physics is concerned with the fundamental nature of matter. The central focuses of this area of study are the relationship between a quantity of energy and its mass, given by $E = mc^2$, and the fact that matter can be converted from one form (energy) to another (particulate) in particle accelerators. Collisions between high-speed particles have produced a dazzling array of new particles—hundreds of them. These events can best be interpreted as conversions of kinetic energy into particles. For example, a collision of sufficient energy between a proton and a neutron can produce four particles: two protons, one antiproton, and a neutron:



where ${}^1_{-1}\text{H}$ is the symbol for an *antiproton*, which has the same mass as a proton but the opposite charge. This process is a little like throwing one baseball at a very high speed into another and having the energy of the collision converted into two additional baseballs.

The results of such accelerator experiments have led scientists to postulate the existence of three types of forces important in the nucleus: the *strong force*, the *weak force*, and the *electromagnetic force*. Along with the *gravitational force*, these forces are thought to account for all types of interactions found in matter. These forces are believed to be generated by the exchange of particles between the interacting pieces of matter. For example, gravitational forces are

thought to be carried by particles called *gravitons*. The electromagnetic force (the classical electrostatic force between charged particles) is assumed to be exerted through the exchange of *photons*. The strong force, not charge-related and effective only at very short distances ($\sim 10^{-13}$ cm), is postulated to involve the exchange of particles called *gluons*. The weak force is 100 times weaker than the strong force and seems to be exerted through the exchange of two types of large particles, the W (has a mass 70 times the proton mass) and the Z (has a mass 90 times the proton mass).

The particles discovered have been classified into several categories. Three of the most important classes are as follows:

1. *Hadrons* are particles that respond to the strong force and have internal structure.
2. *Leptons* are particles that do not respond to the strong force and have no internal structure.
3. *Quarks* are particles with no internal structure that are thought to be the fundamental constituents of hadrons. Neutrons and protons are hadrons that are thought to be composed of three quarks each.

The world of particle physics appears mysterious and complicated. For example, particle physicists have discovered new properties of matter they call “color,” “charm,” and “strangeness” and have postulated conservation laws in-



(left) An aerial view of Fermilab, a high-energy particle accelerator in Batavia, Illinois. (right) The accelerator tunnel at Fermilab.



volving these properties. This area of science is extremely important because it should help us to understand the interactions of matter in a more elegant and unified way. For example, the classification of force into four categories is probably necessary only because we do not understand the true nature of forces. All forces may be special cases of a single, all-pervading force field that governs all of nature. In fact, Einstein spent the last 30 years of his life looking

for a way to unify the gravitational and electromagnetic forces—without success. Physicists may now be on the verge of accomplishing what Einstein failed to do.

Although the practical aspects of the work in nuclear physics are not yet totally apparent, a more fundamental understanding of the way nature operates could lead to presently undreamed-of devices for energy production and communication, which could revolutionize our lives.

Key Terms

neutron
proton
nucleon
atomic number
mass number
isotopes
nuclide

Section 18.1

thermodynamic stability
kinetic stability
radioactive decay
beta (β) particle
zone of stability
alpha (α) particle
 α -particle production
spontaneous fission
 β -particle production
gamma (γ) ray
positron production
electron capture
decay series

Section 18.2

rate of decay
half-life

Section 18.3

nuclear transformation
particle accelerator
cyclotron
linear accelerator
transuranium elements

Section 18.4

Geiger–Müller counter
(Geiger counter)
scintillation counter
radiocarbon dating
(carbon-14 dating)
radiotracers

damage from radiation is proportional to the dose, even at low levels of exposure. Thus any exposure is dangerous. The threshold model, on the other hand, assumes that no significant damage occurs below a certain exposure, called the *threshold exposure*. Note that if the linear model is correct, radiation exposure should be limited to a bare minimum (ideally at the natural levels). If the threshold model is correct, a certain level of radiation exposure beyond natural levels can be tolerated. Most scientists feel that since there is little evidence available to evaluate these models, it is safest to assume that the linear hypothesis is correct and to minimize radiation exposure.

For Review

Summary

The stability of the nucleus, which is composed of neutrons and protons, can be considered from kinetic and thermodynamic points of view. Nuclei that are kinetically unstable decompose into more stable nuclei by radioactive decay, which can involve production of an α particle (${}^4_2\text{He}$), which changes both A and Z , production of a β particle (${}^0_{-1}\text{e}$), which increases Z , or production of a positron (${}^0_1\text{e}$), which decreases Z . High-energy photons called γ rays also can be produced.

A radioactive nuclide may undergo a number of decay events, called a decay series, until a stable nuclide is formed. Radioactive decay follows first-order kinetics. The half-life of a radioactive sample is the time required for the amount of the nuclide to reach half the original amount. The transuranium elements, those coming after uranium in the periodic table, can be synthesized by particle bombardment of uranium or heavier elements.

Radiocarbon dating uses the ratio ${}^{14}_6\text{C}/{}^{12}_6\text{C}$ to date any object containing carbon from living sources.

The thermodynamic stability of the nucleus involves a comparison of the energy of the nucleus to that of its component nucleons. When a system gains or loses energy, it also gains or loses a quantity of mass, given by the relationship $E = mc^2$. The change in mass, called the mass defect, can be obtained by comparing the nuclear mass to the sum of the masses of the component nucleons and

Section 18.5

mass defect
binding energy

Section 18.6

fusion
fission
chain reaction
subcritical reaction
critical reaction
supercritical reaction
critical mass
reactor core
moderator
control rods
breeder reactor

Section 18.7

somatic damage
genetic damage
rad
rem

can be used to calculate the energy of formation of a nucleus from its nucleons. The binding energy is the energy required to decompose the nucleus into protons and neutrons.

Nuclear fusion is the process of combining two light nuclei to form a heavier, more stable nucleus. Fission is the splitting of a heavy nucleus into two lighter nuclei. Nuclear reactors now in use employ controlled fission.

Radiation damage can cause either direct damage to living organisms or genetic damage to the organism's offspring. The biologic effects of radiation depend on the energy, the penetrating ability, and the ionizing ability of the radiation, and on the chemical properties of the radiation source.

A blue question or exercise number indicates that the answer to that question or exercise appears at the back of this book and a solution appears in the *Solutions Guide*.

Questions

1. Define *fission* and *fusion*. Fusion processes are more likely to occur for lighter elements, whereas fission processes are more likely to occur for heavier elements. Explain.
2. When nuclei undergo nuclear transformations, γ rays of characteristic frequencies are observed. How does this fact, along with other information in the chapter on nuclear stability, suggest that a quantum mechanical model may apply to the nucleus?
3. What assumptions must be made and what problems arise in using carbon-14 dating?
4. How could a radioactive nuclide be used to demonstrate that chemical equilibrium is a dynamic process?
5. There is a trend in the United States toward using coal-fired power plants to generate electricity rather than building new nuclear fission power plants. Is the use of coal-fired power plants without risk? Make a list of the risks to society from the use of each type of power plant.
6. Explain why, although gamma rays are far more penetrating than alpha particles, the latter are more likely to cause damage to an organism. Which type of radiation is more effective at causing ionization of biomolecules?
7. Why are elevated temperatures necessary to initiate fusion reactions but not fission reactions?
8. What are the purposes of the moderator and of the control rods in a fission reactor?

Exercises

In this section similar exercises are paired.

Radioactive Decay and Nuclear Transformations

9. Write balanced equations for each of the processes described below.
 - a. Chromium-51, which targets the spleen and is used as a tracer in studies of red blood cells, decays by electron capture.
 - b. Iodine-131, used to treat hyperactive thyroid glands, decays by producing a β particle.
10. Write balanced equations for each of the processes described below.
 - a. Phosphorus-32, which accumulates in the liver, decays by β -particle production.
 - b. Uranium-235, which is used in atomic bombs, decays initially by α -particle production.
11. Write an equation describing the radioactive decay of each of the following nuclides. (The particle produced is shown in parentheses, except for electron capture, where an electron is a reactant.)

a. ^{68}Ga (electron capture)	c. ^{212}Fr (α)
b. ^{62}Cu (positron)	d. ^{129}Sb (β)
12. In each of the following nuclear reactions, supply the missing particle.

a. $^{73}\text{Ga} \rightarrow ^{73}\text{Ge} + ?$	c. $^{205}\text{Bi} \rightarrow ^{205}\text{Pb} + ?$
b. $^{192}\text{Pt} \rightarrow ^{188}\text{Os} + ?$	d. $^{241}\text{Cm} + ? \rightarrow ^{241}\text{Am}$
13. The radioactive isotope ^{247}Bk decays by a series of α -particle and β -particle productions, taking ^{247}Bk through many trans-

formations to end up as ^{207}Pb . In the complete decay series, how many α particles and β particles are produced?

14. One type of commercial smoke detector contains a minute amount of radioactive americium-241 (^{241}Am), which decays by α -particle production. The α particles ionize molecules in the air, allowing it to conduct an electric current. When smoke particles enter, the conductivity of the air is changed and the alarm buzzes.
 - a. Write the equation for the decay of $^{241}_{95}\text{Am}$ by α -particle production.
 - b. The complete decay of ^{241}Am involves successively α , α , β , α , β , α , α , β , α , and β production. What is the final stable nucleus produced in this decay series?
 - c. Identify the 11 intermediate nuclides.

15. There are four stable isotopes of iron with mass numbers 54, 56, 57, and 58. There are also two radioactive isotopes: iron-53 and iron-59. Predict modes of decay for these two isotopes. (See Table 18.2.)

16. The only stable isotope of fluorine is fluorine-19. Predict possible modes of decay for fluorine-21, fluorine-18, and fluorine-17.

17. In 1994 it was proposed that element 106 be named seaborgium, Sg, in honor of Glenn T. Seaborg, discoverer of the transuranium elements.

- a. ^{263}Sg was produced by the bombardment of ^{249}Cf with a beam of ^{18}O nuclei. Complete and balance an equation for this reaction.
- b. ^{263}Sg decays by α emission. What is the other product resulting from the α decay of ^{263}Sg ?

18. Many elements have been synthesized by bombarding relatively heavy atoms with high-energy particles in particle accelerators. Complete the following nuclear reactions, which have been used to synthesize elements.

- a. $\text{_____} + {}^4_2\text{He} \rightarrow {}^{243}_{97}\text{Bk} + {}^1_0\text{n}$
- b. ${}^{238}_{92}\text{U} + {}^{12}_6\text{C} \rightarrow \text{_____} + 6 {}^1_0\text{n}$
- c. ${}^{249}_{98}\text{Cf} + \text{_____} \rightarrow {}^{260}_{105}\text{Db} + 4 {}^1_0\text{n}$
- d. ${}^{249}_{98}\text{Cf} + {}^{10}_5\text{B} \rightarrow {}^{257}_{103}\text{Lr} + \text{_____}$

Kinetics of Radioactive Decay

19. The rate constant for a certain radioactive nuclide is $1.0 \times 10^{-3} \text{ h}^{-1}$. What is the half-life of this nuclide?
20. Americium-241 is widely used in smoke detectors. The radiation released by this element ionizes particles that are then detected by a charged-particle collector. The half-life of ^{241}Am is 432.2 years, and it decays by emitting alpha particles. How many alpha particles are emitted each second by a 5.00-g sample of ^{241}Am ?

21. Krypton consists of several radioactive isotopes, some of which are listed in the following table.

	Half-life
Kr-73	27 s
Kr-74	11.5 min
Kr-76	14.8 h
Kr-81	$2.1 \times 10^5 \text{ yr}$

Which of these isotopes is most stable and which isotope is "hottest"? How long does it take for 87.5% of each isotope to decay?

22. Radioactive copper-64 decays with a half-life of 12.8 days.
 - a. What is the value of k in s^{-1} ?
 - b. A sample contains 28.0 mg ^{64}Cu . How many decay events will be produced in the first second? Assume the atomic mass of ^{64}Cu is 64.0.
 - c. A chemist obtains a fresh sample of ^{64}Cu and measures its radioactivity. She then determines that to do an experiment, the radioactivity cannot fall below 25% of the initial measured value. How long does she have to do the experiment?

23. Phosphorus-32 is a commonly used radioactive nuclide in biochemical research, particularly in studies of nucleic acids. The half-life of phosphorus-32 is 14.3 days. What mass of phosphorus-32 is left from an original sample of 175 mg of $\text{Na}_3^{32}\text{PO}_4$ after 35.0 days? Assume the atomic mass of ^{32}P is 32.0.

24. The curie (Ci) is a commonly used unit for measuring nuclear radioactivity: 1 curie of radiation is equal to 3.7×10^{10} decay events per second (the number of decay events from 1 g of radium in 1 s).
 - a. What mass of $\text{Na}_2^{38}\text{SO}_4$ has an activity of 10.0 mCi? Sulfur-38 has an atomic mass of 38.0 and a half-life of 2.87 h.
 - b. How long does it take for 99.99% of a sample of sulfur-38 to decay?

25. The first atomic explosion was detonated in the desert north of Alamogordo, New Mexico, on July 16, 1945. What fraction of the strontium-90 ($t_{1/2} = 28.8$ years) originally produced by that explosion still remains as of July 16, 2003?

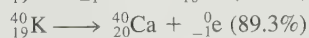
26. Iodine-131 is used in the diagnosis and treatment of thyroid disease and has a half-life of 8.1 days. If a patient with thyroid disease consumes a sample of Na^{131}I containing 10 μg of ^{131}I , how long will it take for the amount of ^{131}I to decrease to 1/100 of the original amount?

27. A living plant contains approximately the same fraction of carbon-14 as in atmospheric carbon dioxide. Assuming that the observed rate of decay of carbon-14 from a living plant is 13.6 counts per minute per gram of carbon, how many counts per minute per gram of carbon will be measured from a 15,000-year-old sample? Will radiocarbon dating work well for small samples of 10 mg or less? (For ^{14}C , $t_{1/2} = 5730$ years.)

28. At a flea market, you've found a very interesting painting done in the style of Rembrandt's "dark period" (1642–1672). You suspect that you really do not have a genuine Rembrandt, but you take it to the local university for testing. Living wood shows a carbon-14 activity of 15.3 counts per minute per gram. Your painting showed a carbon-14 activity of 15.1 counts per minute per gram. Could it be a genuine Rembrandt?

29. A rock contains 0.688 mg of ^{206}Pb for every 1.000 mg of ^{238}U present. Assuming that no lead was originally present, that all the ^{206}Pb formed over the years has remained in the rock, and that the number of nuclides in intermediate stages of decay between ^{238}U and ^{206}Pb is negligible, calculate the age of the rock. (For ^{238}U , $t_{1/2} = 4.5 \times 10^9$ years.)

30. The mass ratios of ^{40}Ar to ^{40}K also can be used to date geological materials. Potassium-40 decays by two processes:



- Why are $^{40}\text{Ar}/^{40}\text{K}$ ratios used to date materials rather than $^{40}\text{Ca}/^{40}\text{K}$ ratios?
- What assumptions must be made using this technique?
- A sedimentary rock has an $^{40}\text{Ar}/^{40}\text{K}$ ratio of 0.95. Calculate the age of the rock.
- How will the measured age of a rock compare to the actual age if some ^{40}Ar escaped from the sample?

Energy Changes in Nuclear Reactions

31. The sun radiates 3.9×10^{23} J of energy into space every second. What is the rate at which mass is lost from the sun?

32. The earth receives 1.8×10^{14} kJ/s of solar energy. What mass of solar material is converted to energy over a 24-h period to provide the daily amount of solar energy to the earth? What mass of coal would have to be burned to provide the same amount of energy? (Coal releases 32 kJ of energy per gram when burned.)

33. Many transuranium elements, such as plutonium-232, have very short half-lives. (For ^{232}Pu , the half-life is 36 minutes.) However, some, like protactinium-231 (half-life = 3.34×10^4 years), have relatively long half-lives. Use the masses given below to calculate the change in energy when one mol of ^{232}Pu nuclei and one mol of ^{231}Pa nuclei are each formed from their respective number of protons and neutrons.

Atom or Particle	Atomic Mass
Neutron	1.67493×10^{-24} g
Proton	1.67262×10^{-24} g
Electron	9.10939×10^{-28} g
Pu-232	3.85285×10^{-22} g
Pa-231	3.83616×10^{-22} g

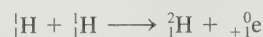
(Since the masses of ^{232}Pu and ^{231}Pa are atomic masses, they each include the mass of the electrons present. The mass of the nucleus will be the atomic mass minus the mass of the electrons.)

34. The most stable nucleus in terms of binding energy per nucleon is ^{56}Fe . If the atomic mass of ^{56}Fe is 55.9349 amu, calculate the binding energy per nucleon for ^{56}Fe .

35. Calculate the binding energy in J/nucleon for carbon-12 (atomic mass 12.0000) and uranium-235 (atomic mass 235.0439). The atomic mass of ^1_1H is 1.00782 amu and the mass of a neutron is 1.00866 amu. The most stable nucleus known is ^{56}Fe (see Exercise 34). Would the binding energy per nucleon for ^{56}Fe be larger or smaller than that of ^{12}C or ^{235}U ? Explain.

36. Calculate the binding energy per nucleon for ^2_1H and ^3_1H . The atomic masses are ^2_1H , 2.01410, and ^3_1H , 3.01605.

37. Calculate the amount of energy released per gram of hydrogen nuclei reacted for the following reaction. The atomic masses are ^1_1H , 1.00782 amu, ^2_1H , 2.01410 amu, and an electron, 5.4858×10^{-4} amu. (Hint: Think carefully about how to account for the electron mass.)



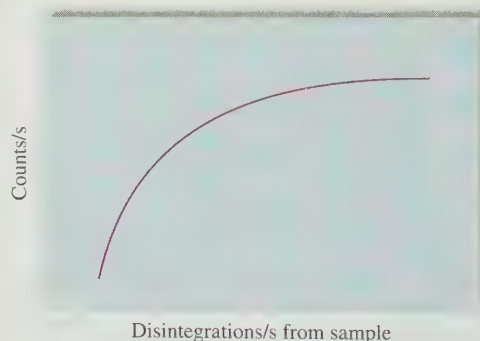
38. The easiest fusion reaction to initiate is



Calculate the energy released per ^4_2He nucleus produced and per mole of ^4_2He produced. The atomic masses are ^2_1H , 2.01410, ^3_1H , 3.01605, and ^4_2He , 4.00260. The masses of the electron and neutron are 5.4858×10^{-4} and 1.00866 amu, respectively.

Detection, Uses, and Health Effects of Radiation

39. The typical response of a Geiger–Müller tube is shown below. Explain the shape of this curve.



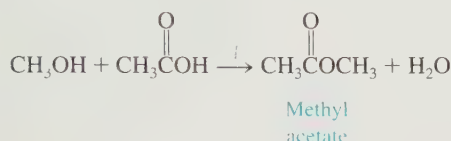
40. When using a Geiger–Müller counter to measure radioactivity, it is necessary to maintain the same geometrical orientation between the sample and the Geiger–Müller tube to compare different measurements. Why?

41. Photosynthesis in plants can be represented by the following overall reaction:



Algae grown in water containing some ^{18}O (in H_2^{18}O) evolve oxygen gas with the same isotopic composition as the oxygen in the water. When algae growing in water containing only ^{16}O were furnished carbon dioxide containing ^{18}O , no ^{18}O was found to be evolved from the oxygen gas produced. What conclusions about photosynthesis can be drawn from these experiments?

42. Consider the following reaction to produce methyl acetate:



When this reaction is carried out with CH_3OH containing oxygen-18, the water produced does not contain oxygen-18. Explain.

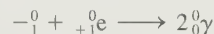
43. Which do you think would be the greater health hazard: the release of a radioactive nuclide of Sr or a radioactive nuclide of Xe into the environment? Assume the amount of radioactivity is the same in each case. Explain your answer on the basis of the chemical properties of Sr and Xe. Why are the chemical properties of a radioactive substance important in assessing its potential health hazards?
44. Consider the following information:
- The layer of dead skin on our bodies is sufficient to protect us from most α -particle radiation.
 - Plutonium is an α -particle producer.
 - The chemistry of Pu^{4+} is similar to that of Fe^{3+} .
 - Pu oxidizes readily to Pu^{4+} .
- Why is plutonium one of the most toxic substances known?

Additional Exercises

45. Predict whether each of the following nuclides is stable or unstable (radioactive). If the nuclide is unstable, predict the type of radioactivity you would expect it to exhibit.
- a. $^{45}_{19}\text{K}$ b. $^{56}_{26}\text{Fe}$ c. $^{20}_{11}\text{Na}$ d. $^{194}_{81}\text{Tl}$
46. A proposed system for storing nuclear wastes involves storing the radioactive material in caves or deep mine shafts. One of the most toxic nuclides that must be disposed of is plutonium-239, which is produced in breeder reactors and has a half-life of 24,100 years. A suitable storage place must be geologically stable long enough for the activity of plutonium-239 to decrease to 0.1% of its original value. How long is this for plutonium-239?
47. During World War II, tritium (^3H) was a component of fluorescent watch dials and hands. Assume you have such a watch that was made in January 1944. If 17% or more of the orig-

inal tritium was needed to read the dial in dark places, until what year could you read the time at night? (For ^3H , $t_{1/2} = 12.3 \text{ yr.}$)

48. A positron and an electron can annihilate each other on colliding, producing energy as photons:



Assuming that both γ rays have the same energy, calculate the wavelength of the electromagnetic radiation produced.

49. A small atomic bomb releases energy equivalent to the detonation of 20,000 tons of TNT; a ton of TNT releases $4 \times 10^9 \text{ J}$ of energy when exploded. Using $2 \times 10^{13} \text{ J/mol}$ as the energy released by fission of ^{235}U , approximately what mass of ^{235}U undergoes fission in this atomic bomb?
50. During the research that led to production of the two atomic bombs used against Japan in World War II, different mechanisms for obtaining a supercritical mass of fissionable material were investigated. In one type of bomb, a "gun" shot one piece of fissionable material into a cavity containing another piece of fissionable material. In the second type of bomb, the fissionable material was surrounded with a high explosive that, when detonated, compressed the fissionable material into a smaller volume. Discuss what is meant by critical mass, and explain why the ability to achieve a critical mass is essential to sustaining a nuclear reaction.

Challenge Problems

51. A 0.10-cm^3 sample of a solution containing a radioactive nuclide (5.0×10^3 counts per minute per milliliter) is injected into a rat. Several minutes later 1.0 cm^3 of blood is removed. The blood shows 48 counts per minute of radioactivity. Calculate the volume of blood in the rat. What assumptions must be made in performing this calculation?
52. Zirconium is one of the few metals that retains its structural integrity upon exposure to radiation. The fuel rods in most nuclear reactors therefore are often made of zirconium. Answer the following questions about the redox properties of zirconium based on the half-reaction



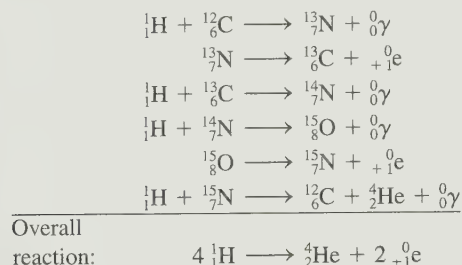
- Is zirconium metal capable of reducing water to form hydrogen gas at standard conditions?
- Write a balanced equation for the reduction of water by zirconium.
- Calculate $\mathcal{E}^\circ$, ΔG° , and K for the reduction of water by zirconium metal.
- The reduction of water by zirconium occurred during the accidents at Three Mile Island in 1979. The hydrogen produced was successfully vented and no chemical explosion occurred. If $1.00 \times 10^3 \text{ kg}$ of Zr reacts, what mass of H_2 is produced? What volume of H_2 at 1.0 atm and $1000.^\circ\text{C}$ is produced?

- e. At Chernobyl in 1986, hydrogen was produced by the reaction of superheated steam with the graphite reactor core:



It was not possible to prevent a chemical explosion at Chernobyl. In light of this, do you think it was a correct decision to vent the hydrogen and other radioactive gases into the atmosphere at Three Mile Island? Explain.

53. In addition to the process described in the text, a second process called the *carbon–nitrogen cycle* occurs in the sun:



- What is the catalyst in this process?
 - What nucleons are intermediates?
 - How much energy is released per mole of hydrogen nuclei in the overall reaction? (The atomic masses of ${}^1_1\text{H}$ and ${}^4_2\text{He}$ are 1.00782 and 4.00260, respectively.)
54. The most significant source of natural radiation is radon-222. ${}^{222}\text{Rn}$, a decay product of ${}^{238}\text{U}$, is continuously generated in the earth's crust allowing gaseous Rn to seep into the basements of buildings. Because ${}^{222}\text{Rn}$ is an α -particle producer with a relatively short half-life of 3.82 days, it can cause biological damage when inhaled.
- How many α particles and β particles are produced when ${}^{238}\text{U}$ decays to ${}^{222}\text{Rn}$? What nuclei is produced when ${}^{222}\text{Rn}$ decays?
 - Radon is a noble gas so one would expect it to pass through the body quickly. Why is there a concern over inhaling ${}^{222}\text{Rn}$?
 - Another problem associated with ${}^{222}\text{Rn}$ is that the decay of ${}^{222}\text{Rn}$ produces a more potent α -particle producer ($t_{1/2} = 3.11 \text{ min}$) that is a solid. What is the identity of the solid?

Give the balanced equation of this species decaying by α -particle production. Why is the solid a more potent α -particle producer?

- d. The U.S. Environmental Protection Agency (EPA) recommends that ${}^{222}\text{Rn}$ levels not exceed 4 pCi per liter of air (1 Ci = 1 curie = 3.7×10^{10} decay events per second; 1 pCi = 1×10^{-12} Ci). Convert 4.0 pCi per liter of air into concentrations units of ${}^{222}\text{Rn}$ atoms per liter of air and mol of ${}^{222}\text{Rn}$ per liter of air.
55. To determine the K_{sp} value of Hg_2I_2 , a chemist obtained a solid sample of Hg_2I_2 in which some of the iodine is present as radioactive ${}^{131}\text{I}$. The count rate of the Hg_2I_2 sample is 5.0×10^{11} counts per minute per mol of I. An excess amount of $\text{Hg}_2\text{I}_2(s)$ is placed into some water, and the solid is allowed to come to equilibrium with its respective ions. A 150.0-mL sample of the saturated solution is withdrawn and the radioactivity measured at 33 counts per minute. From this information, calculate the K_{sp} value for Hg_2I_2 .



Media Activities

- Chapter 18 introduces nuclear chemistry, including radioactive decay, balancing nuclear reactions, kinetics of nuclear decay, uses of nuclear decay, energy changes in nuclear reactions, nuclear fission and fusion reactions, and effects of radiation. Read the Overview on the student CD to review these topics.
- Test your understanding of Chapter 18 material by taking the ACE quizzes on the student web site.



For additional web activities and other resources, visit the Zumdahl, *Chemistry*, Sixth Edition textbook site at <http://chemistry.college.hmco.com/students>.



The Representative Elements: Groups 1A Through 4A

So far in this book we have covered the major principles and explored the most important models of chemistry. In particular, we have seen that the chemical properties of the elements can be explained very successfully by the quantum mechanical model of the atom. In fact, the most convincing evidence of that model's validity is its ability to relate the observed periodic properties of the elements to the number of valence electrons in their atoms.

We have learned many properties of the elements and their compounds, but we have not discussed in detail the relationship between the chemical properties of a particular element and its position on the periodic table. In this chapter and the next we will explore the chemical similarities and differences among the elements in the several groups of the periodic table and will try to interpret these data using the quantum mechanical model of the atom. In the process we will illustrate a great variety of chemical properties and further demonstrate the practical importance of chemistry.

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- 19.1 A Survey of the Representative Elements**
 - Atomic Size and Group Anomalies
 - Abundance and Preparation
- 19.2 The Group 1A Elements**
- 19.3 Hydrogen**
- 19.4 The Group 2A Elements**
- 19.5 The Group 3A Elements**
- 19.6 The Group 4A Elements**

19.1 A Survey of the Representative Elements

The heavy black line in Fig. 19.1 divides the metals from the nonmetals. Some elements just on either side of this line, such as silicon and germanium, exhibit both metallic and nonmetallic properties and are often called **metalloids** or **semimetals**. The fundamental chemical difference between a metal and a nonmetal is that metals tend to lose their valence electrons to form *cations*, usually with the valence-electron configuration of the noble gas from the preceding period, and nonmetals tend to

The periodic table. The elements in the A groups are the representative elements. The elements shown in pink are called *transition metals*. The dark line approximately divides the nonmetals from the metals. The elements that have both metallic and nonmetallic properties (semimetals) are shaded in blue.

Lanthanides	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Actinides	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Metallic character increases going down a group in the periodic table.

gain electrons to form *anions* that exhibit the electron configuration of the noble gas in the same period. Metallic character is observed to increase going down a given group, which is consistent with the trends in ionization energy, electron affinity, and electronegativity discussed earlier (see Sections 7.13 and 8.2).

Atomic Size and Group Anomalies

Although the chemical properties of the members of a group show many similarities, there are also important differences. In fact, the relatively large increase in atomic radius in going from the first to the second member of a group causes the first element to show properties that are often quite different from the others. Consequently, hydrogen, beryllium, boron, carbon, nitrogen, oxygen, and fluorine all have some properties that distinguish them from the other members of their groups. For example, in Group 1A hydrogen is a nonmetal and lithium is a very active metal. This extreme difference results primarily from the very large difference in the atomic radii of hydrogen and lithium, as shown in Fig. 19.2. The small hydrogen atom has

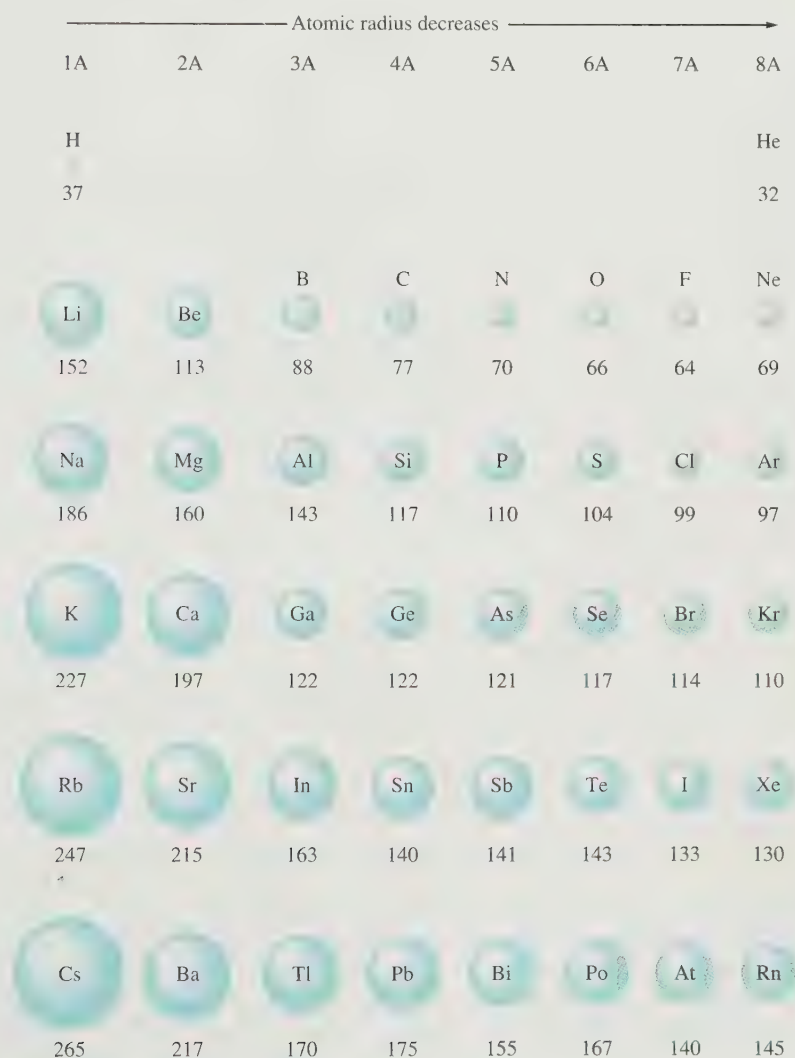


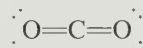
FIGURE 19.2
The atomic radii of some atoms in picometers.

a much greater attraction for electrons than do the larger members of Group 1A and forms covalent bonds with nonmetals; the other members of Group 1A lose their valence electrons to nonmetals to form $1+$ cations in ionic compounds.

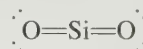
This effect of size is also evident in other groups. For example, the oxides of the metals in Group 2A are all quite basic except for the first member of the series; beryllium oxide (BeO) is amphoteric. Recall from Section 14.10 that the basicity of an oxide depends on its ionic character. Ionic oxides contain the O^{2-} ion, which reacts with water to form two OH^- ions. All the oxides of the Group 2A metals are highly ionic except for beryllium oxide, which has considerable covalent character. The small Be^{2+} ion can effectively polarize the electron “cloud” of the O^{2-} ion, producing significant electron sharing. We see the same pattern in Group 3A, where only the small boron atom behaves as a nonmetal, or sometimes as a semimetal, and aluminum and the other members are active metals.

In Group 4A the effect of size is reflected in the dramatic differences between the chemistry of carbon and that of silicon. The chemistry of carbon is dominated by molecules containing chains of C—C bonds, but silicon compounds mainly contain Si—O bonds rather than Si—Si bonds. Carbon forms a wide variety of stable compounds with strong C—C single bonds. Silicon also forms compounds with chains of Si—Si bonds, but these compounds are much more reactive than the corresponding carbon compounds. The reasons for the difference in reactivity between the carbon and silicon compounds are quite complex but are likely related to the differences in the sizes of the carbon and silicon atoms.

Carbon and silicon differ markedly in their abilities to form π bonds. As we discussed in Section 9.1, carbon dioxide is composed of discrete CO_2 molecules with the Lewis structure



where the carbon and oxygen atoms achieve the $[\text{Ne}]$ configuration by forming π bonds. In contrast, the structure of silica (empirical formula SiO_2) is based on SiO_4 tetrahedra with Si—O—Si bridges, as shown in Fig. 19.3. The silicon $3p$ valence orbitals do not overlap very effectively with the smaller oxygen $2p$ orbitals to form π bonds; therefore, discrete SiO_2 molecules with the Lewis structure



are not stable. Instead, the silicon atoms achieve a noble gas configuration by forming several Si—O single bonds.

The importance of π bonding for the relatively small elements of the second period also explains the different elemental forms of the members of Groups 5A and 6A. For example, elemental nitrogen consists of very stable N_2 molecules with the Lewis structure



Elemental phosphorus forms larger aggregates of atoms, the simplest being the tetrahedral P_4 molecules found in white phosphorus (see Fig. 20.12). Like silicon atoms, the relatively large phosphorus atoms do not form strong π bonds and prefer to achieve a noble gas configuration by forming single bonds to several other phosphorus atoms. In contrast, its very strong π bonds make the N_2 molecule the most stable form of elemental nitrogen. Similarly, in Group 6A the most stable form of elemental oxygen is the O_2 molecule with a double bond, but the larger sulfur atom

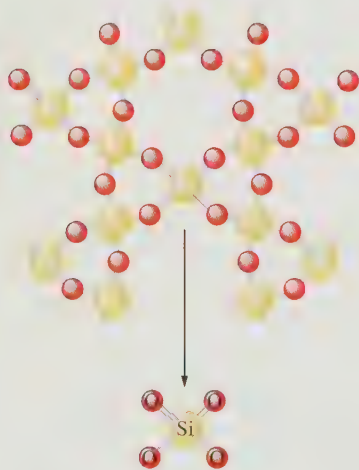


FIGURE 19.3

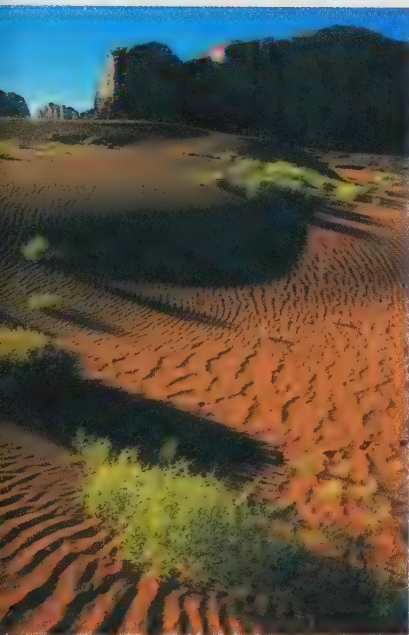
The structure of quartz, which has the empirical formula SiO_2 . Note that the structure is based on interlocking SiO_4 tetrahedra, where each oxygen atom is shared by two silicon atoms.

forms bigger aggregates, such as the cyclic S_8 molecule (see Fig. 20.16), which contains only single bonds.

The relatively large change in size in going from the first to second member of a group also has important consequences for the Group 7A elements. For example, fluorine has a smaller electron affinity than chlorine. This reversal of the expected trend can be attributed to the small fluorine $2p$ orbitals, which result in unusually large electron repulsions. The relative weakness of the bond in the F_2 molecule can be explained in terms of the repulsions among the lone pairs, shown in the Lewis structure:



The small size of the fluorine atoms allows close approach of the lone pairs, which leads to much greater repulsions than are found in the Cl_2 molecule with its much larger atoms.



Sand dunes in Monument Valley, Arizona.

Abundance and Preparation

Table 19.1 shows the distribution of elements in the earth's crust, oceans, and atmosphere. The major element is, of course, oxygen, which is found in the atmosphere as O_2 , in the oceans in H_2O , and in the earth's crust primarily in silicate and carbonate minerals. The second most abundant element, silicon, is found throughout the earth's crust in the silica and silicate minerals that form the basis of most sand, rocks, and soil. The most abundant metals, aluminum and iron, are found in ores in which they are combined with nonmetals, most commonly oxygen. One notable fact revealed by Table 19.1 is the small incidence of most transition metals. Since many of these relatively rare elements are assuming increasing importance in our high-technology society, it is possible that the control of transition metal ores may ultimately have more significance for world politics than the control of petroleum supplies.

The distribution of elements in living materials is very different from that found in the earth's crust. Table 19.2 shows the relative abundance of elements in the human body. Oxygen, carbon, hydrogen, and nitrogen form the basis for all biologically important molecules. The other elements, even though they are found in relatively small amounts, are often crucial for life. For example, zinc is found in over 150 different biomolecules in the human body.

TABLE 19.1 Distribution (Mass Percent) of the 18 Most Abundant Elements in the Earth's Crust, Oceans, and Atmosphere

Element	Mass Percent	Element	Mass Percent
Oxygen	49.2	Chlorine	0.19
Silicon	25.7	Phosphorus	0.11
Aluminum	7.50	Manganese	0.09
Iron	4.71	Carbon	0.08
Calcium	3.39	Sulfur	0.06
Sodium	2.63	Barium	0.04
Potassium	2.40	Nitrogen	0.03
Magnesium	1.93	Fluorine	0.03
Hydrogen	0.87	All others	0.49
Titanium	0.58		

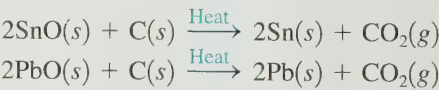
TABLE 19.2 Abundance of Elements in the Human Body

Major Elements	Mass Percent	Trace Elements (in alphabetical order)
Oxygen	65.0	Arsenic
Carbon	18.0	Chromium
Hydrogen	10.0	Cobalt
Nitrogen	3.0	Copper
Calcium	1.4	Fluorine
Phosphorus	1.0	Iodine
Magnesium	0.50	Manganese
Potassium	0.34	Molybdenum
Sulfur	0.26	Nickel
Sodium	0.14	Selenium
Chlorine	0.14	Silicon
Iron	0.004	Vanadium
Zinc	0.003	

Metallurgy is discussed in more detail in Chapter 21.

Carbon is the cheapest and most readily available industrial reducing agent for metallic ions.

Only about one-fourth of the elements occur naturally in the free state. Most are found in a combined state. The *process of obtaining a metal from its ore* is called **metallurgy**. Since the metals in ores are found in the form of cations, the chemistry of *metallurgy always involves reduction of the ions to the elemental metal (with an oxidation state of zero)*. A variety of reducing agents can be used, but carbon is the usual choice because of its wide availability and relatively low cost. As we will see in Chapter 21, carbon is the primary reducing agent in the production of steel. Carbon also can be used to produce tin and lead from their oxides:



Hydrogen gas also can be used as a reducing agent for metal oxides, as in the production of tin:



Electrolysis is often used to reduce the most active metals. In Chapter 17 we considered the electrolytic production of aluminum metal. The alkali metals are also produced by electrolysis, usually of their molten halide salts.

The preparation of nonmetals varies widely. Elemental nitrogen and oxygen are usually obtained from the **liquefaction** of air, which is based on the principle that a real gas cools when it expands. After each expansion, part of the cooler gas is compressed, while the rest is used to carry away the heat of the compression. The compressed gas is then allowed to expand again. This cycle is repeated many times. Eventually, the remaining gas becomes cold enough to form the liquid state. Because liquid nitrogen and liquid oxygen have different boiling points, they can be separated by the distillation of liquid air. Both substances are important industrial chemicals, ranking in the top five in terms of the amounts manufactured in the United States. Hydrogen can be obtained from the electrolysis of water, but more commonly it is obtained from the decomposition of the methane in natural gas. Sulfur is found underground in its elemental form and is recovered using the Frasch process (see Section 20.6). The halogens are obtained by oxidation of the anions from halide salts (see Section 20.7).

The preparation of sulfur and the halogens is discussed in Chapter 20.

19.2 The Group 1A Elements

Several properties of the alkali metals are given in Table 7.8.

1A
H
Li
Na
K
Rb
Cs
Fr

The Group 1A elements with their ns^1 valence-electron configurations are all very active metals (they lose their valence electrons very readily), except for hydrogen, which behaves as a nonmetal. We will discuss the chemistry of hydrogen in the next section. Many of the properties of the **alkali metals** have been described previously (see Section 7.13). The sources and methods of preparation of pure alkali metals are given in Table 19.3. The ionization energies, standard reduction potentials, ionic radii, and melting points for the alkali metals are listed in Table 19.4. Lepidolite, shown in Fig. 19.4, contains several pure alkali metals.

In Section 7.13 we saw that the alkali metals all react vigorously with water to release hydrogen gas:



We will reconsider this process briefly because it illustrates several important concepts. Based on the ionization energies, we might expect lithium to be the weakest of the alkali metals as a reducing agent in water. However, the standard reduction potentials indicate that it is the strongest. This reversal results mainly from the very large energy of hydration of the small Li^+ ion. Because of its relatively high charge density, the Li^+ ion very effectively attracts water molecules. A large quantity of energy is released in the process, favoring the formation of the Li^+ ion and making lithium a strong reducing agent in aqueous solution.

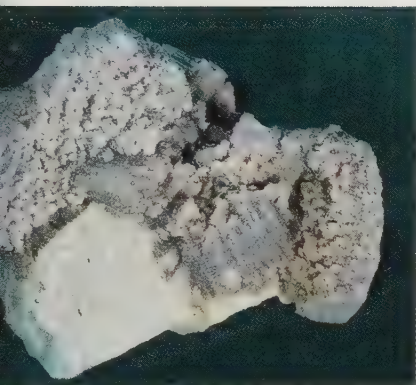


FIGURE 19.4

Lepidolite is composed mainly of lithium, aluminum, silicon, and oxygen, but it also contains significant amounts of rubidium and cesium.

TABLE 19.3 Sources and Methods of Preparation of the Pure Alkali Metals

Element	Source	Method of Preparation
Lithium	Silicate minerals such as spodumene, $LiAl(Si_2O_6)$	Electrolysis of molten $LiCl$
Sodium	$NaCl$	Electrolysis of molten $NaCl$
Potassium	KCl	Electrolysis of molten KCl
Rubidium	Impurity in lepidolite, $Li_2(F,OH)_2Al_2(SiO_3)_3$	Reduction of $RbOH$ with Mg and H_2
Cesium	Pollucite ($Cs_4Al_4Si_9O_{26} \cdot H_2O$) and an impurity in lepidolite (see Fig. 19.4)	Reduction of $CsOH$ with Mg and H_2

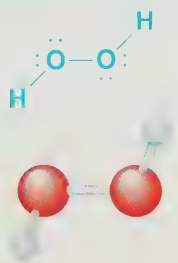
TABLE 19.4 Selected Physical Properties of the Alkali Metals

Element	Ionization Energy (kJ/mol)	Standard Reduction Potential (V) for $M^+ + e^- \rightarrow M$	Radius of M^+ (pm)	Melting Point ($^{\circ}C$)
Lithium	520	-3.05	60	180
Sodium	495	-2.71	95	98
Potassium	419	-2.92	133	63
Rubidium	409	-2.99	148	39
Cesium	382	-3.02	169	29



Sodium reacting with water.

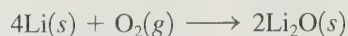
Hydrogen peroxide has the Lewis structure



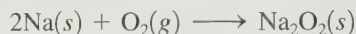
Airpacks are an essential source of oxygen for firefighters.

We also saw in Section 7.13 that lithium, although it is the strongest reducing agent, reacts more slowly with water than does sodium or potassium. From the discussions in Chapters 12 and 16, we know that the *equilibrium position* for a reaction (in this case indicated by the $\mathcal{E}^\circ$ values) is controlled by thermodynamic factors but that the *rate* of a reaction is controlled by kinetic factors. There is *no* direct connection between these factors. Lithium reacts more slowly with water than does sodium or potassium because as a solid it has a higher melting point than either of them. It does not become molten from the heat of reaction with water as sodium and potassium do, and thus it has a smaller area of contact with the water.

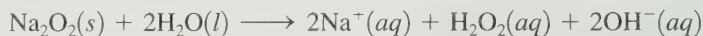
The relative ease with which the alkali metals lose electrons to form M^+ cations means that they react with nonmetals to form ionic compounds. Although we might expect the alkali metals to react with oxygen to form regular oxides of the general formula M_2O , lithium is the only one that does so in the presence of excess oxygen gas:



Sodium forms solid Na_2O if the oxygen supply is limited, but in excess oxygen it forms *sodium peroxide*:

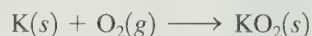


Sodium peroxide contains the basic O_2^{2-} anion and reacts with water to form hydrogen peroxide and hydroxide ions:

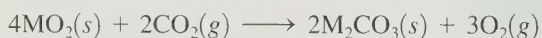
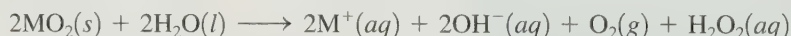


Hydrogen peroxide is a strong oxidizing agent often used as a bleach for hair and as a disinfectant.

Potassium, rubidium, and cesium react with oxygen to produce **superoxides** of the general formula MO_2 , which contains the O_2^- anion. For example, potassium reacts with oxygen as follows:



The superoxides release oxygen gas in reactions with water or carbon dioxide:



This chemistry makes superoxides very useful in the self-contained breathing apparatuses used by firefighters. These “airpacks” are also used as emergency equipment in labs and production facilities in case toxic fumes are released.

The types of compounds formed by the alkali metals with oxygen are summarized in Table 19.5. Table 19.6 summarizes some important reactions of the alkali metals.

TABLE 19.5 Types of Compounds Formed by the Alkali Metals with Oxygen

General Formula	Name	Examples
M_2O	Oxide	Li_2O , Na_2O
M_2O_2	Peroxide	Na_2O_2
MO_2	Superoxide	KO_2 , RbO_2 , CsO_2



Sodium reacts violently with chlorine.

TABLE 19.6 Selected Reactions of the Alkali Metals

Reaction	Comment
$2M + X_2 \rightarrow 2MX$	X_2 = any halogen molecule
$4Li + O_2 \rightarrow 2Li_2O$	Excess oxygen
$2Na + O_2 \rightarrow Na_2O_2$	
$M + O_2 \rightarrow MO_2$	$M = K, Rb, \text{ or } Cs$
$2M + S \rightarrow M_2S$	
$6Li + N_2 \rightarrow 2Li_3N$	Li only
$12M + P_4 \rightarrow 4M_3P$	
$2M + H_2 \rightarrow 2MH$	
$2M + 2H_2O \rightarrow 2MOH + H_2$	
$2M + 2H^+ \rightarrow 2M^+ + H_2$	Violent reaction!

The alkali metal ions are very important for the proper functioning of biologic systems, such as nerves and muscles, and Na^+ and K^+ ions are present in all body cells and fluids. In human blood plasma the concentrations are

$$[Na^+] \approx 0.15 \text{ M} \quad \text{and} \quad [K^+] \approx 0.005 \text{ M}$$

For the fluids *inside* the cells the concentrations are reversed:

$$[Na^+] \approx 0.005 \text{ M} \quad \text{and} \quad [K^+] \approx 0.16 \text{ M}$$

Since the concentrations are so different inside and outside the cells, an elaborate mechanism is needed to transport Na^+ and K^+ ions through the cell membranes.

Recently, studies have been carried out concerning the role of the Li^+ ion in the human brain, and lithium carbonate has been used extensively in the treatment of manic-depressive patients. The Li^+ ion apparently affects the levels of neurotransmitters, molecules that assist the transmission of messages along the nerve networks. Incorrect concentrations of these molecules can lead to depression or mania.

SAMPLE EXERCISE 19.1

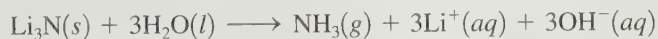
Predicting Reaction Products

Predict the products formed by the following reactants.

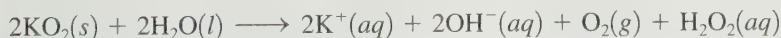
- $Li_3N(s)$ and $H_2O(l)$
- $KO_2(s)$ and $H_2O(l)$

SOLUTION

- Solid Li_3N contains the N^{3-} anion, which has a strong attraction for three H^+ ions to form NH_3 . Thus the reaction is



- Solid KO_2 is a superoxide that characteristically reacts with water to produce O_2 , H_2O_2 , and OH^- :

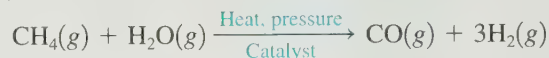


See Exercises 19.17 and 19.18.

19.3 Hydrogen

Under ordinary conditions of temperature and pressure, hydrogen is a colorless, odorless gas composed of H_2 molecules. Because of its low molar mass and nonpolarity, hydrogen has a very low boiling point (-253°C) and melting point (-260°C). Hydrogen gas is highly flammable, and mixtures of air containing from 18% to 60% hydrogen by volume are explosive. In a common lecture demonstration hydrogen and oxygen gases are bubbled into soapy water. The resulting bubbles can be ignited with a candle on a long stick, giving a loud explosion.

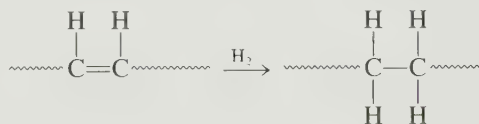
The major industrial source of hydrogen gas, is the reaction of methane and water at high temperatures ($800\text{--}1000^\circ\text{C}$) and high pressures (10–50 atm) with a metallic catalyst, often nickel:



Large quantities of hydrogen are also formed as a by-product of gasoline production, in which hydrocarbons with high molar masses are broken down (*cracked*) to produce smaller molecules more suitable for use as a motor fuel.

Very pure hydrogen can be produced by electrolysis of water (see Section 17.7), but this method is currently not economically feasible for large-scale production because of the relatively high cost of electricity.

The major industrial use of hydrogen is in the production of ammonia by the Haber process. Large quantities of hydrogen are also used for hydrogenating unsaturated vegetable oils (those containing carbon–carbon double bonds) to produce solid shortenings that are saturated (containing carbon–carbon single bonds):



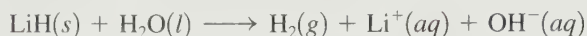
The catalysis of this process was discussed in Section 12.8.

Chemically, hydrogen behaves as a typical nonmetal, forming covalent compounds with other nonmetals and forming salts with very active metals. Binary compounds containing hydrogen are called **hydrides**, of which there are three classes.

(left) Hydrogen gas being used to blow soap bubbles. (right) As the bubbles float upward, they are lighted using a candle on a long pole. The orange flame is due to the heat from the reaction of hydrogen with the oxygen in the air that excites sodium ions in the soap solution.



The **ionic** (or **saltlike**) **hydrides** are formed when hydrogen combines with the most active metals, those from Groups 1A and 2A. Examples are LiH and CaH₂, which can best be characterized as containing hydride ions (H⁻) and metal cations. Because the presence of two electrons in the small 1s orbital produces large electron–electron repulsions and the nucleus only has a 1+ charge, the hydride ion is a strong reducing agent (easily loses electrons). For example, when ionic hydrides are placed in water, a violent reaction takes place. This reaction results in the formation of hydrogen gas, as seen in the equation



Boiling points of covalent hydrides are discussed in Section 10.1.

Covalent hydrides are formed when hydrogen combines with other nonmetals. We have encountered many of these compounds already: HCl, CH₄, NH₃, H₂O, and so on. The most important covalent hydride is water. The polarity of the H₂O molecule leads to many of water's unusual properties. Water has a much higher boiling point than is expected from its molar mass. It has a large heat of vaporization and a large heat capacity, both of which make it a very useful coolant. Water has a higher density as a liquid than as a solid. This is due to the open structure of ice, which results from maximizing the hydrogen bonding (see Fig. 19.5). Because water is an excellent solvent for ionic and polar substances, it provides an effective medium for life processes. In fact, water is one of the few covalent hydrides that is nontoxic to organisms.

The third class of hydrides, the **metallic** (or **interstitial**) **hydrides**, are formed when transition metal crystals are treated with hydrogen gas. The hydrogen molecules dissociate at the metal's surface, and the small hydrogen atoms migrate into the crystal structure to occupy holes, or interstices. These metal–hydrogen mixtures are more like solid solutions than true compounds. Palladium can absorb about 900 times its own volume of hydrogen gas. In fact, hydrogen can be purified by placing it under slight pressure in a vessel containing a thin wall of palladium. The hydrogen diffuses into and through the metal wall, leaving the impurities behind.

Although hydrogen can react with transition metals to form compounds of constant composition, most of the interstitial hydrides have variable compositions (often called *nonstoichiometric compositions*) with formulas such as LaH_{2.76} and VH_{0.56}. The compositions of the nonstoichiometric hydrides vary with the length of exposure of the metal to hydrogen gas and other factors.

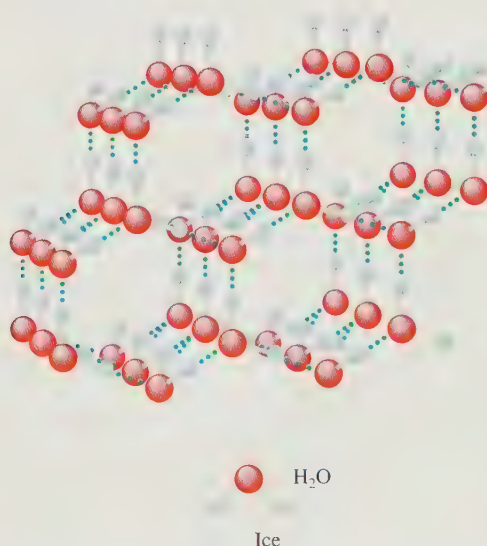


FIGURE 19.5
The structure of ice, showing the hydrogen bonding.

See Section 6.6 for a discussion of the feasibility of using hydrogen gas as a fuel.

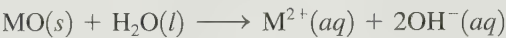
An amphoteric oxide displays both acidic and basic properties.

When interstitial hydrides are heated, much of the absorbed hydrogen is expelled as hydrogen gas. Because of this behavior, these materials offer possibilities for storing hydrogen for use as a portable fuel. The internal combustion engines in current automobiles can burn hydrogen gas with little modification, but storage of enough hydrogen to provide an acceptable mileage range remains a problem. One possible solution might be to use a fuel tank containing a porous solid that includes a transition metal into which the hydrogen gas could be pumped to form the interstitial hydride. The hydrogen gas could then be released as required by the engine.

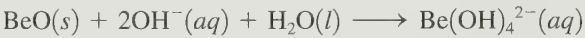
19.4 The Group 2A Elements

2A
Be
Mg
Ca
Sr
Ba
Ra

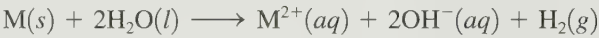
The Group 2A elements (with valence-electron configuration ns^2) are very reactive, losing their two valence electrons to nonmetals to form ionic compounds containing M^{2+} cations. These elements are commonly called the **alkaline earth metals** because of the basicity of their oxides:



Only beryllium oxide (BeO) also shows some acidic properties, such as dissolving in aqueous solutions containing hydroxide ions:



The more active alkaline earth metals react with water as the alkali metals do, producing hydrogen gas:



Calcium, strontium, and barium react vigorously at 25°C . The less easily oxidized beryllium and magnesium show no observable reaction with water at 25°C , although magnesium reacts with boiling water. Table 19.7 summarizes various properties, sources, and preparations of the alkaline earth metals.

TABLE 19.7 Selected Physical Properties, Sources, and Methods of Preparation for the Group 2A Elements

Element	Radius of M^{2+} (pm)	Ionization Energy (kJ/mol)		$E^\circ(V)$ for $M^{2+} + 2e^- \rightarrow M$	Source	Method of Preparation
		First	Second			
Beryllium	~30	900	1760	-1.70	Beryl ($Be_3Al_2Si_6O_{18}$)	Electrolysis of molten $BeCl_2$
Magnesium	65	738	1450	-2.37	Magnesite ($MgCO_3$), dolomite ($MgCO_3 \cdot CaCO_3$), carnallite ($MgCl_2 \cdot KCl \cdot 6H_2O$)	Electrolysis of molten $MgCl_2$
Calcium	99	590	1146	-2.76	Various minerals containing $CaCO_3$	Electrolysis of molten $CaCl_2$
Strontium	113	549	1064	-2.89	Celestite ($SrSO_4$), strontianite ($SrCO_3$)	Electrolysis of molten $SrCl_2$
Barium	135	503	965	-2.90	Baryte ($BaSO_4$), witherite ($BaCO_3$)	Electrolysis of molten $BaCl_2$
Radium	140	509	979	-2.92	Pitchblende (1 g of Ra/7 tons of ore)	Electrolysis of molten $RaCl_2$



Calcium metal reacting with water to form bubbles of hydrogen gas.

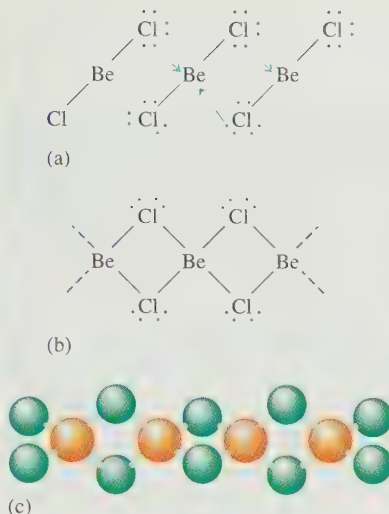
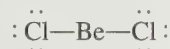


FIGURE 19.6

(a) Solid BeCl_2 can be visualized as being formed from many BeCl_2 molecules, where lone pairs on the chlorine atoms are used to bond to the beryllium atoms in adjacent BeCl_2 molecules. (b) The extended structure of solid BeCl_2 . (c) The ball-and-stick model of the extended structure.

As we saw in Section 19.1, the small size and relatively high electronegativity of the beryllium atom cause its bonds to be more covalent than is usual for a metal. For example, beryllium chloride with the Lewis structure



exists as a linear molecule, as predicted by the VSEPR model. The Be—Cl bonds are covalent, and beryllium is best described as being sp hybridized. As a solid, BeCl_2 achieves an octet of electrons around each beryllium atom by forming an extended structure containing Be in a tetrahedral environment, as shown in Fig. 19.6. The lone pairs on the chlorine atoms are used to form Be—Cl bonds.

The alkaline earth metals have great practical importance. Calcium and magnesium ions are essential for human life. Calcium is found primarily in the structural minerals constituting bones and teeth; magnesium (as the Mg^{2+} ion) plays a vital role in metabolism and muscle functions. Also, magnesium was formerly used to produce the bright light for photographic flash bulbs from its reaction with oxygen:



Because magnesium metal has a relatively low density and moderate strength, it is a useful structural material, especially if alloyed with aluminum.

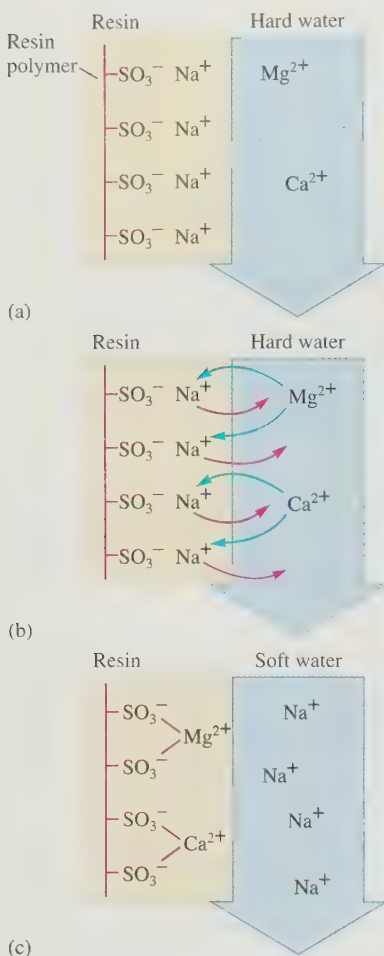
Table 19.8 summarizes some important reactions of the alkaline earth metals.

TABLE 19.8 Selected Reactions of the Group 2A Elements

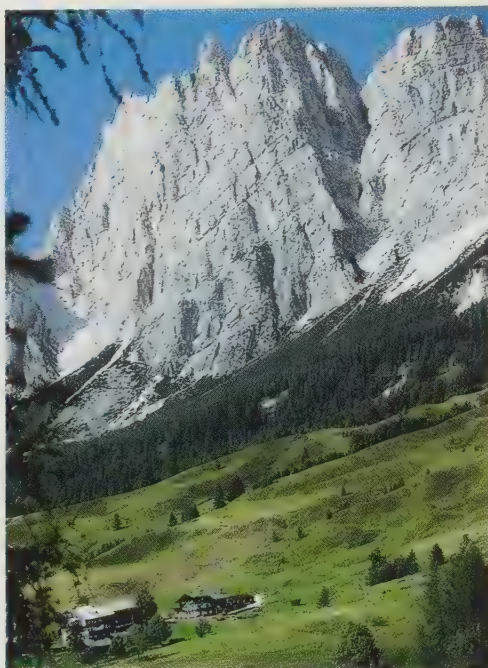
Reaction	Comment
$\text{M} + \text{X}_2 \rightarrow \text{MX}_2$	$\text{X}_2 = \text{any halogen molecule}$
$2\text{M} + \text{O}_2 \rightarrow 2\text{MO}$	Ba gives BaO_2 as well
$\text{M} + \text{S} \rightarrow \text{MS}$	
$3\text{M} + \text{N}_2 \rightarrow \text{M}_3\text{N}_2$	High temperatures
$6\text{M} + \text{P}_4 \rightarrow 2\text{M}_3\text{P}_2$	High temperatures
$\text{M} + \text{H}_2 \rightarrow \text{MH}_2$	$\text{M} = \text{Ca, Sr, or Ba; high temperatures; Mg at high pressure}$
$\text{M} + 2\text{H}_2\text{O} \rightarrow \text{M}(\text{OH})_2 + \text{H}_2$	$\text{M} = \text{Ca, Sr, or Ba}$
$\text{M} + 2\text{H}^+ \rightarrow \text{M}^{2+} + \text{H}_2$	
$\text{Be} + 2\text{OH}^- + 2\text{H}_2\text{O} \rightarrow \text{Be}(\text{OH})_4^{2-} + \text{H}_2$	



Bones contain large amounts of calcium.

**FIGURE 19.7**

(a) A schematic representation of a typical cation-exchange resin. (b) and (c) When hard water is passed over the cation-exchange resin, the Ca^{2+} and Mg^{2+} bind to the resin.



The Dolomite mountains in Italy. Dolomite is a source of magnesium.

Relatively large concentrations of Ca^{2+} and Mg^{2+} ions are often found in natural water supplies. These ions in this **hard water** interfere with the action of detergents and form precipitates with soap. In Section 14.6 we saw that Ca^{2+} is often removed by precipitation as CaCO_3 in large-scale water softening. In individual homes Ca^{2+} , Mg^{2+} , and other cations are removed by **ion exchange**. An **ion-exchange resin** consists of large molecules (polymers) that have many ionic sites. A **cation-exchange resin** is represented schematically in Fig. 19.7(a), showing Na^+ ions bound ionically to the SO_3^- groups that are covalently attached to the resin polymer. When hard water is passed over the resin, Ca^{2+} and Mg^{2+} bind to the resin in place of Na^+ , which is released into the solution [Fig. 19.7(b)]. Replacing Mg^{2+} and Ca^{2+} by Na^+ [Fig. 19.7(c)] “softens” the water because the sodium ions interfere much less with the action of soaps and detergents.

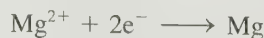
SAMPLE EXERCISE 19.2

Electrolytic Production of Magnesium

Calculate the amount of time required to produce 1.00×10^3 kg of magnesium metal by the electrolysis of molten MgCl_2 using a current of 1.00×10^2 A.

SOLUTION

The reaction for plating magnesium is



which means that 2 moles of electrons are required for each mole of Mg produced. The number of moles of magnesium in 1.00×10^3 kg is

$$1.00 \times 10^3 \text{ kg} \times \frac{1000 \text{ g}}{\text{kg}} \times \frac{1 \text{ mol Mg}}{24.31 \text{ g}} = 4.11 \times 10^4 \text{ mol Mg}$$



Visualization: Dry Ice and Magnesium

$$\text{Thus } \frac{2 \text{ mol e}^-}{1 \text{ mol Mg}} \times 4.11 \times 10^4 \text{ mol Mg} = 8.22 \times 10^4 \text{ mol e}^-$$

Using the faraday (96,485 C/mol e⁻), we can calculate the coulombs of charge:

$$8.22 \times 10^4 \text{ mol e}^- \times \frac{96,485 \text{ C}}{\text{mol e}^-} = 7.93 \times 10^9 \text{ C}$$

Since an ampere is a coulomb of charge per second, we can now calculate the time required:

$$\frac{7.93 \times 10^9 \text{ C}}{1.00 \times 10^2 \text{ C/s}} = 7.93 \times 10^7 \text{ s} \quad \text{or} \quad 918 \text{ days}$$

See Exercises 19.29 and 19.30.

19.5 The Group 3A Elements

3A
B
Al
Ga
In
Tl

The Group 3A elements (valence-electron configuration ns^2np^1) generally show the increase in metallic character in going down the group that is characteristic of the representative elements. Some physical properties, sources, and methods of preparation for the Group 3A elements are summarized in Table 19.9.

Boron is a nonmetal, and most of its compounds are covalent. The most interesting compounds of boron are the covalent hydrides called **boranes**. We might expect BH_3 to be the simplest hydride, since boron has three valence electrons to share with three hydrogen atoms. However, this compound is unstable, and the simplest known member of the series is diborane (B_2H_6), with the structure shown in Fig. 19.8(a). In this molecule the terminal B—H bonds are normal covalent bonds, each involving one electron pair. The bridging bonds are three-center bonds using a single pair of electrons to bond all three atoms. Another interesting borane contains

TABLE 19.9 Selected Physical Properties, Sources, and Methods of Preparation for the Group 3A Elements

Element	Radius of M^{3+} (pm)	Ionization Energy (kJ/mol)	$E^\circ(\text{V})$ for $\text{M}^{3+} + 3\text{e}^- \rightarrow \text{M}$	Sources	Method of Preparation
Boron	20	798	—	Kernite, a form of borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$)	Reduction by Mg or H_2
Aluminum	51	581	-1.71	Bauxite (Al_2O_3)	Electrolysis of Al_2O_3 in molten Na_3AlF_6
Gallium	62	577	-0.53	Traces in various minerals	Reduction with H_2 or electrolysis
Indium	81	556	-0.34	Traces in various minerals	Reduction with H_2 or electrolysis
Thallium	95	589	0.72	Traces in various minerals	Electrolysis

CHEMICAL IMPACT

Boost Your Boron

Everyone realizes that the body needs protein, carbohydrates, vitamins, and even fat. The importance of several trace elements in our diet, however, is often poorly understood. An example is the element boron. People in the United States have a relatively low intake of boron. For example, the U.S. population consumes a little more than 1 mg of boron per day, which is about 10% less than people living in Great Britain and Egypt and about 35% less than people in Germany and Mexico.

To study the importance of boron intake, Zuo-Fen Zhang and his colleagues in the School of Public Health at the University of California–Los Angeles examined nutrition data collected from thousands of men and women who filled out the National Health and Nutrition Examination Survey (NHANES). Zhang and his coworkers learned that

boron seems to protect against prostate cancer. Comparing the diets of men with prostate cancer to those without the disease indicated a strong correlation between boron consumption and the absence of the disease. The prostate cancer risk for men eating at least 1.8 mg boron per day was only one-third that of men who consumed less than 0.9 mg boron per day. The data show that boron offers no apparent protection for other types of cancer, just very specific protection for prostate cancer. Other studies involving animals indicate that boron consumption can furnish protection against autoimmune diseases such as rheumatoid arthritis.

Although boron intake in the neighborhood of 3.0 mg/day seems beneficial, large amounts of boron can be toxic. The best way to obtain extra boron in your diet is by consuming foods such as nuts and noncitrus fruits.



Gallium metal has such a low melting point (30°C) that it melts from the heat of a hand.

the square pyramidal B_5H_9 molecule [Fig. 19.8(b)], which has four three-center bonds around the base of the pyramid. Because the boranes are extremely electron-deficient, they are highly reactive. The boranes react very exothermically with oxygen and were once evaluated as potential fuels for rockets in the U.S. space program.

Aluminum, the most abundant metal on earth, has metallic physical properties, such as high thermal and electrical conductivities and a lustrous appearance, but its bonds to nonmetals are significantly covalent. This covalency is responsible for the amphoteric nature of Al_2O_3 , which dissolves in acidic or basic solution, and for the acidity of $Al(H_2O)_6^{3+}$ (see Section 14.8):



One especially interesting property of **gallium** is its unusually low melting point at 29.8°C, which is in contrast to the 660°C melting point of aluminum. Gallium's boiling point is approximately 2400°C. This gives gallium the largest liquid range of any metal, which makes it useful for thermometers, especially to measure high temperatures. Gallium, like water, expands when it freezes. The chemistry of gallium is quite similar to that of aluminum. For example, Ga_2O_3 is amphoteric.

Table 19.10 summarizes some important reactions of the Group 3A elements.

The practical importance of the Group 3A elements centers on aluminum. Since the discovery of the electrolytic production process by Hall and Heroult (see Section 17.8), aluminum has become a highly important structural material in a wide

FIGURE 19.8

(a) The structure of B_2H_6 with its two three-center B—H—B bridging bonds and four “normal” B—H bonds. (b) The structure of B_5H_9 . There are five “normal” B—H bonds to terminal hydrogens and four three-center bridging bonds around the base.





Aluminum is used in airplane construction.

TABLE 19.10 Selected Reactions of the Group 3A Elements

Reaction	Comment
$2M + 3X_2 \rightarrow 2MX_3$	X_2 = any halogen molecule; Tl gives TlX as well, but no TlI_3
$4M + 3O_2 \rightarrow 2M_2O_3$	High temperatures; Tl gives Tl_2O as well
$2M + 3S \rightarrow M_2S_3$	High temperatures; Tl gives Tl_2S as well
$2M + N_2 \rightarrow 2MN$	M = Al only
$2M + 6H^+ \rightarrow 2M^{3+} + 3H_2$	M = Al, Ga, or In; Tl gives Tl^+
$2M + 2OH^- + 6H_2O \rightarrow 2M(OH)_4^- + 3H_2$	M = Al or Ga

variety of applications from aircraft bodies to bicycle components. Aluminum is especially valuable because it has a high strength-to-weight ratio and because it protects itself from corrosion by developing a tough, adherent oxide coating.

19.6 The Group 4A Elements

4A
C
Si
Ge
Sn
Pb

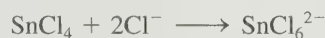
Group 4A (with the valence-electron configuration ns^2np^2) contains two of the most important elements on earth: carbon, the fundamental constituent of the molecules necessary for life, and silicon, which forms the basis of the geologic world. The change from nonmetallic to metallic properties seen in Group 3A is also apparent in going down Group 4A from carbon, a typical nonmetal, to silicon and germanium, usually considered semimetals, to the metals tin and lead. Table 19.11 summarizes some physical properties, sources, and methods of preparation for the elements in this group.

All the Group 4A elements can form four covalent bonds to nonmetals—for example, CH_4 , SiF_4 , $GeBr_4$, $SnCl_4$, and $PbCl_4$. In each of these tetrahedral mole-

TABLE 19.11 Selected Physical Properties, Sources, and Methods of Preparation for the Group 4A Elements

Element	Electronegativity	Melting Point (°C)	Boiling Point (°C)	Sources	Method of Preparation
Carbon	2.5	3727 (sublimes)	—	Graphite, diamond, petroleum, coal	—
Silicon	1.8	1410	2355	Silicate minerals, silica	Reduction of K_2SiF_6 with Al, or reduction of SiO_2 with Mg
Germanium	1.8	937	2830	Germanite (mixture of copper, iron, and germanium sulfides)	Reduction of GeO_2 with H_2 or C
Tin	1.8	232	2270	Cassiterite (SnO_2)	Reduction of SnO_2 with C
Lead	1.9	327	1740	Galena (PbS)	Roasting of PbS with O_2 to form PbO_2 and then reduction with C

cules, the central atom is described as sp^3 hybridized by the localized electron model. All these compounds, except those of carbon, can react with Lewis bases to form two additional covalent bonds. For example, SnCl_4 , which is a fuming liquid (bp = 114°C), can add two chloride ions:



Carbon compounds cannot react in this way because of the small atomic size of carbon and because there are no d orbitals on carbon to accommodate the extra electrons, as there are on the other elements in the group.

We have seen that carbon also differs markedly from the other members of Group 4A in its ability to form π bonds. This accounts for the completely different structures and properties of CO_2 and SiO_2 . Note from Table 19.12 that C—C bonds and Si—O bonds are stronger than Si—Si bonds. This partly explains why the chemistry of carbon is dominated by C—C bonds, whereas that of silicon is dominated by Si—O bonds.

Carbon occurs in the earth's crust mainly in two allotropic forms—graphite and diamond. In addition, new forms of elemental carbon, including buckminsterfullerene (C_{60}) and other related substances, have recently been characterized. The structures of graphite and diamond are given in Section 10.5.

Carbon monoxide (CO), one of three oxides of carbon, is an odorless, colorless, and toxic gas formed as a by-product of the combustion of carbon-containing compounds when there is a limited oxygen supply. Incidents of carbon monoxide poisoning are especially common in the winter in cold areas of the world when blocked furnace vents limit the availability of oxygen. The bonding in carbon monoxide, which has the Lewis structure



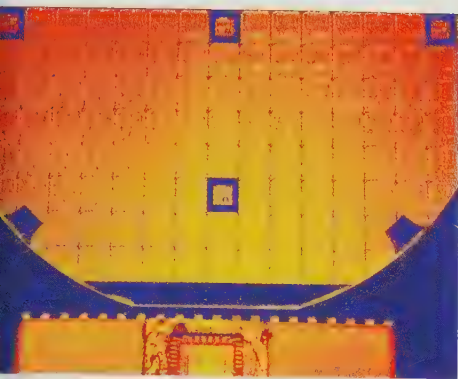
is described in terms of sp hybridized carbon and oxygen atoms that interact to form one σ and two π bonds.

Although graphite is thermodynamically more stable than diamond, the transformation of diamond to graphite is not observed under normal conditions.

Fullerenes have been discovered recently by geologists in ancient rocks in Russia.

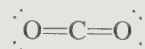
TABLE 19.12 Strengths of C—C, Si—Si, and Si—O Bonds

Bond	Bond Energy (kJ/mol)
C—C	347
Si—Si	340
Si—O	452



(top) A processed silicon wafer with
(bottom) a silicon microchip.

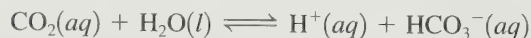
Carbon dioxide, a linear molecule with the Lewis structure



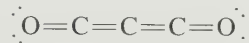
has an *sp* hybridized carbon atom, and is a product of human and animal respiration and of the combustion of fossil fuels. It is also produced by fermentation, a process by which the sugar in fruits and grains is changed to ethanol ($\text{C}_2\text{H}_5\text{OH}$) and carbon dioxide (see Section 22.4):



Carbon dioxide dissolves in water to produce an acidic solution:



Carbon suboxide, the third carbon oxide, is a linear molecule with the Lewis structure



which contains *sp* hybridized carbon atoms.

Silicon, the second most abundant element in the earth's crust, is a semimetal found widely distributed in silica and silicates (see Section 10.5). Approximately 85% of the earth's crust is composed of these substances. Although silicon is found in some steel and aluminum alloys, its major use is in semiconductors for electronic devices (see the Chemical Impact in Section 10.5).

Germanium, a relatively rare element, is a semimetal used mainly in the manufacture of semiconductors for transistors and similar electronic devices.

Tin is a soft silvery metal that can be rolled into thin sheets (tin foil) and has been used for centuries in various alloys such as bronze (~20% Sn and ~80% Cu), solder (~33% Sn and ~67% Pb), and pewter (~85% Sn, ~7% Cu, ~6% Bi, and ~2% Sb). Tin exists as three allotropes: *white tin*, stable at normal temperatures; *gray tin*, stable at temperatures below 13.2°C; and *brittle tin*, found at temperatures above 161°C. When tin is exposed to low temperatures, it gradually changes to the powdery gray tin and crumbles away; this process is known as *tin disease*.

The major current use for tin is as a protective coating for steel, especially for cans used as food containers. The thin layer of tin, applied electrolytically, forms a protective oxide coating that prevents further corrosion.

Lead is easily obtained from its ore, galena (PbS). Because lead melts at such a low temperature, it may have been the first pure metal obtained from its ore. We know that lead was used as early as 3000 B.C. by the Egyptians and was later used by the Romans to make eating utensils, glazes on pottery, and even intricate plumbing systems. Lead is very toxic, however. In fact, the Romans had so much contact with lead that it may have contributed to the demise of their civilization. Analysis of bones from that era shows significant levels of lead.

Although lead poisoning has been known since at least the second century B.C., the incidences of this problem have been relatively isolated. However, the widespread use of tetraethyl lead, $(\text{C}_2\text{H}_5)_4\text{Pb}$, as an antiknock agent in gasoline increased the lead levels in our environment in the twentieth century. Concern about the effects of this lead pollution has caused the U.S. government to require the gradual replacement of the lead in gasoline with other antiknock agents. The largest

The compositions of these alloys vary significantly. For example, the tin content of bronze varies from 5% to 30%, and the tin content of pewter is often as high as 95%.



Roman baths such as these in Bath, England, used lead pipes for water.

CHEMICAL IMPACT

Concrete Learning

Concrete has literally paved the way for civilization over the past 5000 years, tracing its roots to the ancient Egyptians. At a cost of about a penny per pound, concrete is ubiquitous in today's world—used in houses, factories, roads, dams, cooling towers, pipes, skyscrapers, and countless other places. In the United States alone there are an estimated \$6 trillion worth of concrete-based structures.

Most concretes are based on Portland cement, patented in 1824 by an English bricklayer named J. Aspdin and so named because it forms a product that resembles the natural limestone on the Isle of Portland in England. Portland cement is a powder containing a mixture of calcium silicates [Ca_2SiO_4 (26%) and Ca_3SiO_5 (51%)], calcium aluminate [$\text{Ca}_3\text{Al}_2\text{O}_6$ (11%)], and calcium iron aluminate [$\text{Ca}_4\text{Al}_2\text{Fe}_2\text{O}_{10}$ (1%)]. Portland cement is made from a mixture of limestone, sand, shale, clay, and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). When the cement is mixed with sand, gravel, and water, it turns into a muddy substance that eventually hardens into the familiar concrete that finds so many uses in our world. The hardening of concrete occurs not through drying but through hydration. The material becomes dry and hard as the water is consumed in building the complex silicate structures present in cured concrete. Although many of the details of this process are poorly understood, the main “glue” that holds the components of concrete together is calcium silicate hydrate, which forms a three-dimensional network mainly responsible for concrete's strength.

Despite its strength when newly produced, concrete contains pockets of air and water dispersed throughout, making it porous and subject to deterioration. Thus, despite all the ad-

vantages of concrete, it cracks and deteriorates seriously over time.

Much research is now being carried out to improve the durability of concrete. Most of these efforts are directed toward lowering the porosity of concrete and making it less brittle. One group of additives aimed at solving this problem consists of molecules with carbon atom backbones that have sulfate groups attached. These so-called superplasticizers allow the formation of concrete using much less water, and these chemicals have doubled the strength of ready-mix concrete over the past 20 years.

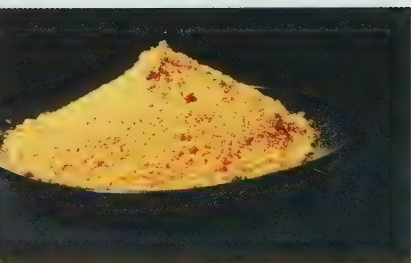
Researchers also have found that the properties of concrete can be greatly improved by adding fibers of various kinds, including those made of steel, glass, and carbon-based polymers. One type of fiber concrete—called *slurry infiltrated fiber concrete* (SIFCON), which is tough enough to be used to make missile silos and can be formed into complex shapes—may be especially useful for structures in earthquake-prone areas.

Other efforts to improve concrete center on replacing Portland cement with other binders such as carbon-based polymers. Although these polymer-based concretes will burn and do lose their shapes at high temperatures, they are much more resistant to the effects of water, acids, and salts than those made with Portland cement.

Despite the fact that most concrete now used is very similar to that used by the Romans to build the Pantheon, progress is being made, and revolutionary improvements may be just around the corner.

commercial use of lead (about 1.3 million tons annually) is for electrodes in the lead storage batteries used in automobiles (see Section 17.5).

Table 19.13 summarizes some important reactions of the Group 4A elements.



Lead(II) oxide, known as *litharge*.

TABLE 19.13 Selected Reactions of the Group 4A Elements

Reaction	Comment
$\text{M} + 2\text{X}_2 \rightarrow \text{MX}_4$	X_2 = any halogen molecule; M = Ge or Sn; Pb gives PbX_2
$\text{M} + \text{O}_2 \rightarrow \text{MO}_2$	M = Ge or Sn; high temperatures; Pb gives PbO or Pb_3O_4
$\text{M} + 2\text{H}^+ \rightarrow \text{M}^{2+} + \text{H}_2$	M = Sn or Pb

CHEMICAL IMPACT

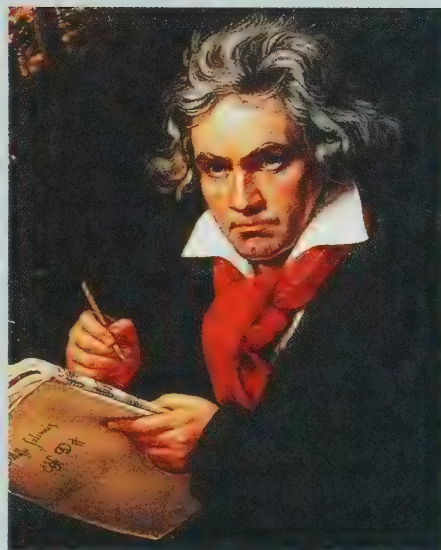
Beethoven: Hair Is the Story

Ludwig van Beethoven, arguably the greatest composer who ever lived, led a troubled life fraught with sickness, deafness, and personality aberrations. Now we may know the source of these difficulties: lead poisoning. Scientists have recently reached this conclusion through analysis of Beethoven's hair. When Beethoven died in 1827 at age 56, many mourners took samples of the great man's hair. In fact, it was said at the time that he was practically bald by the time he was buried. The hair that was recently analyzed consisted of 582 strands—3 to 6 inches long—bought for the Center of Beethoven Studies for \$7300 in 1994 from Sotheby's auction house in London.

According to William Walsh of the Health Research Institute (HRI) in suburban Chicago, Beethoven's hair showed a lead concentration 100 times the normal levels. The scientists concluded that Beethoven's exposure to lead came as an adult, possibly from the mineral water he drank and swam in when he visited spas.

The lead poisoning may well explain Beethoven's volatile temper—the composer was subject to towering rages and sometimes had the look of a wild animal. In rare cases lead poisoning has been known to cause deafness, but the researchers remain unsure if this problem led to Beethoven's hearing loss.

According to Walsh, the scientists at HRI were originally looking for mercury, a common treatment for syphilis in the



Portrait of Beethoven by Josef Kari Stieler.

early nineteenth century, in Beethoven's hair. The absence of mercury supports the consensus of scholars that Beethoven did not have this disease. Not surprisingly, Beethoven himself wanted to know what made him so ill. In a letter to his brothers in 1802, he asked them to have doctors find the cause of his frequent abdominal pain after his death.

For Review

Summary

The representative elements have chemical properties determined by their valence s and p electrons. Although the chemical properties of the members of a group are similar in many ways, there is usually a dramatic difference between the first member and the rest of the group due to size variations. For example, hydrogen in Group 1A is much smaller than lithium and forms covalent bonds because it has a much greater attraction for electrons than do the larger members of Group 1A. The first member of a group forms the strongest π bonds, causing elemental nitrogen and oxygen to exist as N_2 and O_2 molecules, while phosphorus and sulfur exist as P_4 and S_8 molecules.

The most abundant element is oxygen, followed by silicon. The most abundant metals are aluminum and iron, which are found as ores in which they are combined with nonmetals, most commonly oxygen.

The Group 1A elements have the valence-electron configuration ns^1 and lose the one electron readily to form M^+ ions, except for hydrogen, which is a nonmetal.

Key Terms

Section 19.1

representative elements
transition metals
lanthanides
actinides
metalloids (semimetals)
metallurgy
liquefaction

Section 19.2

alkali metals

superoxide

Section 19.3

hydride

ionic (saltlike) hydride

covalent hydride

metallic (interstitial) hydride

Section 19.4

alkaline earth metals

hard water

ion exchange

ion-exchange resin

cation-exchange resin

Section 19.5

boranes

The alkali metals all react vigorously with water to form M^+ and OH^- ions and hydrogen gas. With oxygen they form a series of oxides. The regular oxide is formed by lithium (Li_2O). Sodium forms the peroxide Na_2O_2 in excess oxygen, and potassium, rubidium, and cesium form the superoxides of general formula MO_2 .

Hydrogen can form covalent compounds with other nonmetals and can form salts with very active metals. Hydrogen's binary compounds are called hydrides. Ionic hydrides are formed when hydrogen combines with the Group 1A and Group 2A metals. The hydride ion (H^-) is a strong reducing agent. Covalent hydrides are formed when hydrogen combines with other nonmetals. Metallic hydrides are formed when hydrogen atoms migrate into transition metal crystals.

The Group 2A elements (with the valence-electron configuration ns^2) are called the alkaline earth metals because of the basicity of their oxides. Only the smallest (first) member of the group, beryllium, has an amphoteric oxide. The alkaline earth metals react less vigorously with water than do the alkali metals, with beryllium and magnesium showing no reaction at all at $25^\circ C$. The heavier alkaline earth metals form ionic nitrides and hydrides.

Hard water contains Ca^{2+} and Mg^{2+} ions, which can be removed by precipitation of $CaCO_3$ or by ion-exchange resins. These polymeric molecules have many ionic sites, usually with Na^+ ions bound to them. When hard water is passed over the resin, the Ca^{2+} and Mg^{2+} ions replace Na^+ on the resin, and are removed from the water.

The Group 3A elements (with the valence-electron configuration ns^2np^1) show increasing metallic character going down the group. Boron is a nonmetal that forms covalent hydrides called boranes; these are highly electron-deficient with three-center bonds and are therefore very reactive. Aluminum, a metal, has some covalent characteristics, as do gallium and indium.

The Group 4A elements (with the valence-electron configuration ns^2np^2) also show a change from nonmetallic to metallic properties in going down the group. However, all these elements can form covalent bonds to nonmetals. The MX_4 compounds, except those of carbon, can react with Lewis bases to form two additional covalent bonds; CX_4 compounds cannot react in this way because carbon has no $2d$ orbitals and the $3d$ orbitals are too high in energy to be used.

A blue question or exercise number indicates that the answer to that question or exercise appears at the back of this book and a solution appears in the *Solutions Guide*.

Questions

- Although the earth was formed from the same interstellar material as the sun, there is little elemental hydrogen (H_2) in the earth's atmosphere. Explain.
- List two major industrial uses of hydrogen.
- Name the three types of hydrides. How do they differ?
- Many lithium salts are hygroscopic (absorb water), whereas the corresponding salts of the other alkali metals are not. Explain.
- What evidence supports putting hydrogen in Group 1A of the periodic table? In some periodic tables hydrogen is listed separately from any of the groups. In what ways is hydrogen unlike a typical Group 1A element?
- Describe how potassium superoxide is used in a self-contained breathing apparatus.
- All the Group 1A and 2A metals are produced by electrolysis of molten salts. Why?
- How do the acidities of the aqueous solutions of the alkaline earth metal ions (M^{2+}) change in going down the group?
- Why is graphite a good lubricant? What advantages does it have over grease- or oil-based lubricants?
- What are some of the structural differences between quartz and amorphous SiO_2 ?
- What type of semiconductor is formed when a Group 3A element is added as an impurity to Si or Ge?
- Diagonal relationships in the periodic table exist as well as the vertical relationships. For example, Be and Al are similar in some of their properties as are B and Si. Rationalize why these diagonal relationships hold for properties such as size, ionization energy, and electron affinity.

Exercises

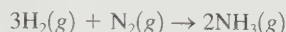
In this section similar exercises are paired.

Group 1A Elements

13. Hydrogen is produced commercially by the reaction of methane with steam:



- Calculate ΔH° and ΔS° for this reaction (use the data in Appendix 4).
 - What temperatures will favor product formation at standard conditions? Assume ΔH° and ΔS° do not depend on temperature.
14. The major industrial use of hydrogen is in the production of ammonia by the Haber process:



- Using data from Appendix 4, calculate ΔH° , ΔS° , and ΔG° for the Haber process reaction.
 - Is the reaction spontaneous at standard conditions?
 - At what temperatures is the reaction spontaneous at standard conditions? Assume ΔH° and ΔS° do not depend on temperature.
15. Name each of the following compounds.
- Li_2O
 - KO_2
 - Na_2O_2
16. Write the formula for each of the following compounds.
- lithium nitride
 - potassium carbonate
 - rubidium hydroxide
 - sodium hydride
17. Complete and balance the following reactions.
- $\text{Li}_2\text{O}(s) + \text{H}_2\text{O}(l) \rightarrow$
 - $\text{Na}_2\text{O}_2(s) + \text{H}_2\text{O}(l) \rightarrow$
 - $\text{LiH}(s) + \text{H}_2\text{O}(l) \rightarrow$
 - $\text{KO}_2(s) + \text{H}_2\text{O}(l) \rightarrow$
18. Write balanced equations describing the reaction of lithium metal with each of the following: O_2 , S_8 , Cl_2 , P_4 , H_2 , H_2O , and HCl .
19. Lithium reacts with acetylene in liquid ammonia to produce LiC_2H (lithium acetylide, $\text{LiC}\equiv\text{CH}$) and hydrogen gas. Write a balanced equation for this reaction. What type of reaction is this?
20. The electrolysis of aqueous sodium chloride (brine) is an important industrial process for the production of chlorine and sodium hydroxide. In fact, this process is the second largest consumer of electricity in the United States, after the production of aluminum. Write a balanced equation for the electrolysis of aqueous sodium chloride (hydrogen gas is also produced).

Group 2A Elements

- Name each of the following compounds.
 - MgCO_3
 - BaSO_4
 - $\text{Sr}(\text{OH})_2$
- Write the formula for each of the following compounds.
 - calcium nitride
 - beryllium chloride
 - barium hydride
- One harmful effect of acid rain is the deterioration of structures and statues made of marble or limestone, both of which are essentially calcium carbonate. The reaction of calcium carbonate with sulfuric acid yields carbon dioxide, water, and calcium sulfate. Because calcium sulfate is marginally soluble in water, part of the object is washed away by the rain. Write a balanced chemical equation for the reaction of sulfuric acid with calcium carbonate.
- Write balanced equations describing the reaction of Sr with each of the following: O_2 , S_8 , Cl_2 , P_4 , H_2 , H_2O , and HCl .
- Predict the structure of BeF_2 in the gas phase. What structure would you predict for $\text{BeF}_2(s)$?
- The beryllium atom in BeCl_2 is electron-deficient (only four valence electrons surround it), which makes it very reactive toward electron-pair donors such as ammonia. Draw a Lewis structure for the expected product when BeCl_2 reacts with excess ammonia.
- The U.S. Public Health Service recommends the fluoridation of water as a means for preventing tooth decay. The recommended concentration is 1 mg F^- per liter. The presence of calcium ions in hard water can precipitate the added fluoride. What is the maximum molarity of calcium ions in hard water if the fluoride concentration is at the USPHS recommended level? (K_{sp} for $\text{CaF}_2 = 4.0 \times 10^{-11}$)
- Slaked lime, $\text{Ca}(\text{OH})_2$, is used to soften hard water by removing calcium ions from hard water through the reaction

$$\text{Ca}(\text{OH})_2(aq) + \text{Ca}^{2+}(aq) + 2\text{HCO}_3^-(aq) \rightarrow 2\text{CaCO}_3(s) + 2\text{H}_2\text{O}(l)$$

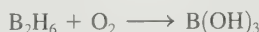
Although $\text{CaCO}_3(s)$ is considered insoluble, some of it does dissolve in aqueous solutions. Calculate the molar solubility of CaCO_3 in water ($K_{\text{sp}} = 8.7 \times 10^{-9}$).
- What mass of barium is produced when molten BaCl_2 is electrolyzed by a current of 2.50×10^5 A for 6.00 hours?
- Electrolysis of an alkaline earth metal chloride using a current of 5.00 A for 748 seconds deposits 0.471 g of metal at the cathode. What is the identity of the alkaline earth metal chloride?

Group 3A Elements

- Write the formula for each of the following compounds.
 - aluminum nitride
 - gallium fluoride
 - gallium sulfide

32. Thallium and indium form +1 and +3 oxidation states when in compounds. Predict the formulas of the possible compounds between thallium and oxygen and between indium and chlorine. Name the compounds.

33. Boron hydrides were once evaluated for possible use as rocket fuels. Complete and balance the following equation for the combustion of diborane.



34. Elemental boron is produced by reduction of boron oxide with magnesium to give boron and magnesium oxide. Write a balanced equation for this reaction.

35. Ga_2O_3 is an amphoteric oxide, and In_2O_3 is a basic oxide. Write equations for the reactions that illustrate these properties.

36. Aluminum hydroxide is amphoteric and will dissolve in both acidic and basic solutions. Write balanced chemical equations representing each process.

37. Write equations describing the reactions of Ga with each of the following: F_2 , O_2 , S_8 , N_2 , and HCl .

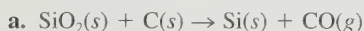
38. Write a balanced equation describing the reaction of aluminum metal with concentrated aqueous sodium hydroxide.

Group 4A Elements

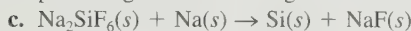
39. Draw Lewis structures for CF_4 , GeF_4 , and GeF_6^{2-} . Predict the molecular structure (including bond angles), and give the expected hybridization of the central atom in these three substances. Explain why CF_6^{2-} does not form.

40. Carbon and sulfur form compounds with the formulas CS_2 and C_3S_2 . Draw Lewis structures and predict the shapes of these two compounds.

41. Silicon is produced for the chemical and electronics industries by the following reactions. Give the balanced equation for each reaction.



b. Silicon tetrachloride is reacted with very pure magnesium, producing silicon and magnesium chloride.



42. Write equations describing the reactions of Sn with each of the following: Cl_2 , O_2 , and HCl .

43. Why are people advised not to drink hot tap water if their plumbing contains lead solder?

44. Calculate the solubility of $\text{Pb}(\text{OH})_2$ ($K_{\text{sp}} = 1.2 \times 10^{-15}$) in water. Is $\text{Pb}(\text{OH})_2$ more or less soluble in acidic solutions? Explain.

45. The fermentation of glucose produces ethanol and carbon dioxide. Write a balanced equation for this reaction.

46. Tin forms compounds in the +2 and +4 oxidation states. Therefore, when tin reacts with fluorine, two products are pos-

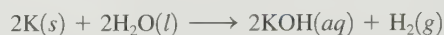
sible. Write balanced equations for the production of the two tin halide compounds and name them.

47. The resistivity (a measure of electrical resistance) of graphite is $(0.4 \text{ to } 5.0) \times 10^{-4} \text{ ohm} \cdot \text{cm}$ in the basal plane. (The basal plane is the plane of the six-membered rings of carbon atoms.) The resistivity is 0.2 to 1.0 $\text{ohm} \cdot \text{cm}$ along the axis perpendicular to the plane. The resistivity of diamond is 10^{14} to $10^{16} \text{ ohm} \cdot \text{cm}$ and is independent of direction. How can you account for this behavior in terms of the structures of graphite and diamond?

48. Silicon carbide (SiC) is an extremely hard substance. Propose a structure for SiC .

Additional Exercises

49. Calculate ΔH° for the reaction



A 5.00-g chunk of potassium is dropped into 1.00 kg of water at 24.0°C . What is the final temperature of the water after the preceding reaction occurs? Assume that all the heat is used to raise the temperature of the water, and assume that the specific heat capacity of the solution is $4.18 \text{ J/}^\circ\text{C} \cdot \text{g}$. (Never run this reaction. It is very dangerous; it bursts into flame!)

50. The bright yellow light emitted by a sodium vapor lamp consists of two emission lines at 589.0 and 589.6 nm. What are the frequency and the energy of a photon of light at each of these wavelengths? What are the energies in kJ/mol?

51. In the 1950s and 1960s, several nations conducted tests of nuclear warheads in the atmosphere. It was customary following each test to monitor the concentration of strontium-90 (a radioactive isotope of strontium) in milk. Why would strontium-90 tend to accumulate in milk?

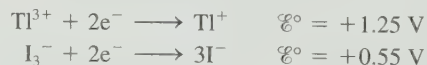
52. The compound $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ cannot be dehydrated easily by heating. It dissolves in water to give an acidic solution. Explain these observations.

53. The inert-pair effect is sometimes used to explain the tendency of heavier members of group 3A to exhibit +1 and +3 oxidation states. What does the inert-pair effect reference? *Hint:* Consider the valence electron configuration for group 3A elements.

54. Assume that element 113 is produced. What is the expected electron configuration for element 113?

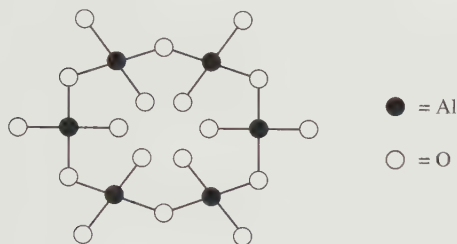
55. Calculate the pH of a 0.050 M $\text{Al}(\text{NO}_3)_3$ solution. The K_{a} value for $\text{Al}(\text{H}_2\text{O})_6^{3+}$ is 1.4×10^{-5} .

56. The compound with the formula TlI_3 is a black solid. Given the following standard reduction potentials:



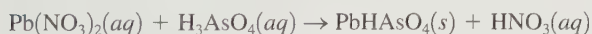
would you formulate this compound as thallium(III) iodide or thallium(I) triiodide?

57. How could you determine experimentally whether the compound Ga_2Cl_4 contains two gallium(II) ions or one gallium(I) and one gallium(III) ion? (*Hint*: Consider the electron configurations of the three possible ions.)
58. Tricalcium aluminate, an important component of Portland cement, is 44.4% calcium and 20.0% aluminum by mass. The remainder is oxygen.
- Calculate the empirical formula of tricalcium aluminate.
 - The structure of tricalcium aluminate was not determined until 1975. The aluminate anion ($\text{Al}_6\text{O}_{18}^{18-}$) has the following structure:



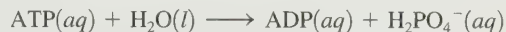
What is the molecular formula of tricalcium aluminate?

- c. How would you describe the bonding in the $\text{Al}_6\text{O}_{18}^{18-}$ anion?
59. In Exercise 103 in Chapter 5, the pressure of CO_2 in a bottle of sparkling wine was calculated assuming that the CO_2 was insoluble in water. This was a bad assumption. Redo this problem by assuming CO_2 obeys Henry's law. Use the data given in that problem to calculate the partial pressure of CO_2 in the gas phase and the solubility of CO_2 in the wine at 25°C . The Henry's law constant for CO_2 is $3.1 \times 10^{-2} \text{ mol/L} \cdot \text{atm}$ at 25°C with Henry's law in the form $C = kP$, where C is the concentration of the gas in mol/L .
60. The compound Pb_3O_4 (red lead) contains a mixture of lead(II) and lead(IV) oxidation states. What is the mole ratio of lead(II) to lead(IV) in Pb_3O_4 ?
61. Lead hydrogen arsenate, an inorganic insecticide used against the potato beetle, is produced by the following reaction:



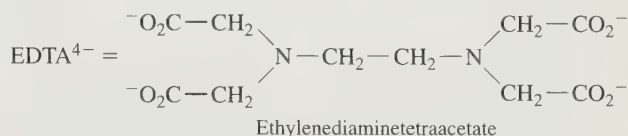
Balance this equation.

- b. When 1.0 mol of K^+ is transferred from blood to the cells, do any other ions have to be transported? Why or why not?
- c. Cells use the hydrolysis of adenosine triphosphate, abbreviated ATP, as a source of energy. Symbolically, this reaction can be represented as



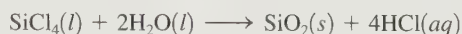
where ADP represents adenosine diphosphate. For this reaction at 37°C, $K = 1.7 \times 10^5$. How many moles of ATP must be hydrolyzed to provide the energy for the transport of 1.0 mol of K^+ ? Assume standard conditions for the ATP hydrolysis reaction.

63. EDTA is used as a complexing agent in chemical analysis. Solutions of EDTA, usually containing the disodium salt $\text{Na}_2\text{H}_2\text{EDTA}$, are also used to treat heavy metal poisoning. The equilibrium constant for the following reaction is 1.0×10^{23} .



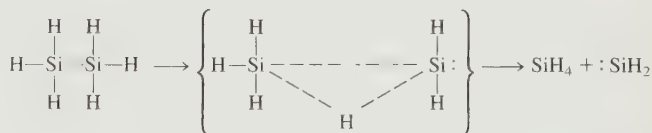
Calculate the $[\text{Pb}^{2+}]$ at equilibrium in a solution originally $0.0010\text{ }M$ in Pb^{2+} , $0.050\text{ }M$ in $\text{H}_2\text{EDTA}^{2-}$, and buffered at $\text{pH} = 6.00$.

64. The compounds CCl_4 and H_2O do not react with each other. On the other hand, silicon tetrachloride reacts with water according to the equation



Discuss the importance of thermodynamics and kinetics in the reactivity of water with SiCl_4 as compared with its lack of reactivity with CCl_4 .

65. One reason suggested to account for the instability of long chains of silicon atoms is that the decomposition involves the transition state shown below:



The activation energy for such a process is 210 kJ/mol, which is less than either the Si—Si or Si—H energy. Why would a similar mechanism not be expected to be very important in the decomposition of long carbon chains?

66. From the information on the temperature stability of white and gray tin given in this chapter, which form would you expect to have the more ordered structure?

Challenge Problems

- 62. a.** Many biochemical reactions that occur in cells require relatively high concentrations of potassium ion (K^+). The concentration of K^+ in muscle cells is about $0.15\ M$. The concentration of K^+ in blood plasma is about $0.0050\ M$. The high internal concentration in cells is maintained by pumping K^+ from the plasma. How much work must be done to transport $1.0\ \text{mol}$ of K^+ from the blood to the inside of a muscle cell at 37°C (normal body temperature)?

Marathon Problem

This problem is designed to incorporate several concepts and techniques into one situation. Marathon Problems can be used in class by groups of students to help facilitate problem-solving skills.

67. Use the symbols of the elements described in the following clues to fill in the blanks that spell out the name of a famous American scientist. Although this scientist was better known as a physicist than as a chemist, the Philadelphia institute that bears his name does include a biochemistry research facility.

(1) _____ (2) _____ (3) _____ (4) _____ (5) _____ (6) _____ (7) _____

- (1) The oxide of this metal is amphoteric.
- (2) You might be surprised to learn that a binary compound of sodium with this element has the formula NaX_3 , a compound used in airbags.
- (3) This alkali metal is radioactive.
- (4) This element is the alkali metal with the least negative standard reduction potential. Write its symbol in reverse order.
- (5) Potash is an oxide of this alkali metal.
- (6) This is the only alkali metal that reacts directly with nitrogen to make a binary compound with formula M_3N .
- (7) This element is the first in Group 3A for which the +1 oxidation state is exhibited in stable compounds. Use only the second letter of its symbol.



Media Activities

1. Chapter 19 presents the Group 1A, 2A, 3A, and 4A elements. The material to emphasize for each group of elements includes the properties discussed, bonding characteristics, and typical reactions. Read the Overview on the Student CD to review important topics covered in Chapter 19.
2. Open the Dry Ice and Magnesium Visualization on the student CD and view the reactions. Magnesium can react with oxygen as well as with carbon dioxide. Write balanced equations for these reactions. (*Hint:* As indicated in the concept, magnesium displaces oxygen in CO_2 , forming magnesium oxide and carbon.)
 - a. What is oxidized and reduced in each reaction?
 - b. Why did the match go out when placed in the beaker of CO_2 ? Sometimes reactions with magnesium can get out of hand. Why shouldn't you use a CO_2 fire extinguisher to put out a magnesium fire?
3. Test your understanding of Chapter 19 material by taking the ACE quizzes on the student web site.



For additional web activities and other resources, visit the Zumdahl, *Chemistry*, Sixth Edition textbook site at <http://chemistry.college.hmco.com/students>.



The Representative Elements: Groups 5A Through 8A

In Chapter 19 we saw that vertical groups of elements tend to show similar chemical characteristics because they have identical valence-electron configurations. Generally, metallic character increases going down a group, as the valence electrons are found farther from the nucleus. Also, recall that the most dramatic change in properties occurs after the first group member, mainly because the most dramatic change in size occurs between the first and second group members.

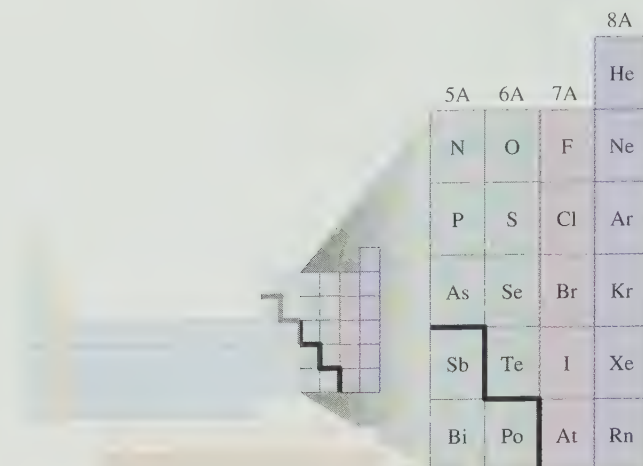
As we proceed from Group 1A to Group 7A, the elements change from active metals (electron donors) to strong nonmetals (electron acceptors). Thus it is not surprising that the middle groups show the most varied chemistry: Some group members behave principally as metals, others behave mainly as nonmetals, and some show both tendencies. The elements in Groups 5A and 6A show great chemical variety and form many compounds of considerable practical value. The halogens (Group 7A) are nonmetals that are also found in many everyday substances such as household bleach, photographic films, and “automatic” sunglasses. The elements in Group 8A (the noble gases) are most useful in their elemental forms, but their ability to form compounds, discovered only within the past 40 years, has provided important tests for the theories of chemical bonding.

In this chapter we give an overview of the elements in Groups 5A through 8A, concentrating on the chemistry of the most important elements in these groups: nitrogen, phosphorus, oxygen, sulfur, and the halogens.

CONTENTS

- 20.1 The Group 5A Elements**
- 20.2 The Chemistry of Nitrogen**
 - Nitrogen Hydrides
 - Nitrogen Oxides
 - Oxyacids of Nitrogen
- 20.3 The Chemistry of Phosphorus**
 - Phosphorus Oxides and Oxyacids
 - Phosphorus in Fertilizers
 - Phosphorus Halides
- 20.4 The Group 6A Elements**
- 20.5 The Chemistry of Oxygen**
- 20.6 The Chemistry of Sulfur**
 - Sulfur Oxides
 - Oxyacids of Sulfur
 - Other Compounds of Sulfur
- 20.7 The Group 7A Elements**
 - Hydrogen Halides
 - Oxyacids and Oxyanions
 - Other Halogen Compounds
- 20.8 The Group 8A Elements**

The carnivorous pitcher plant “eats” insects to utilize the nitrogen held in the insect tissue.



5A	6A	7A	8A
N	O	F	Ne
P	S	Cl	Ar
As	Se	Br	Kr
Sb	Te	I	Xe
Bi	Po	At	Rn

20.1 The Group 5A Elements

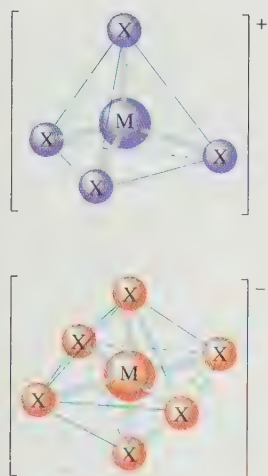
5A
N
P
As
Sb
Bi

The Group 5A elements (with the valence-electron configuration ns^2np^3) are prepared as shown in Table 20.1, and they show remarkably varied chemical properties. As usual, metallic character increases going down the group, as is apparent from the electronegativity values (Table 20.1). *Nitrogen* and *phosphorus* are nonmetals that can gain three electrons to form 3[−] anions in salts with active metals, for example, magnesium nitride (Mg_3N_2) and beryllium phosphide (Be_3P_2). The chemistry of these two important elements is discussed in the next two sections.

Bismuth and *antimony* tend to be metallic, readily losing electrons to form cations. Although these elements have five valence electrons, so much energy is required to remove all five that no ionic compounds containing Bi^{5+} or Sb^{5+} ions are

TABLE 20.1 Selected Physical Properties, Sources, and Methods of Preparation for the Group 5A Elements

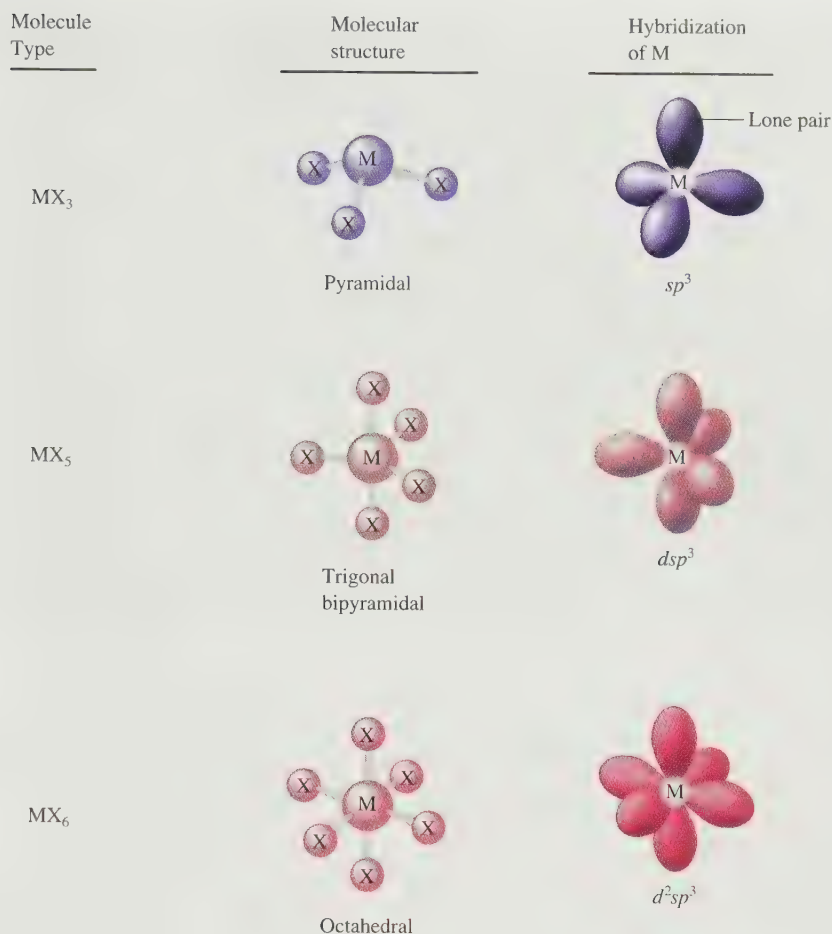
Element	Electro-negativity	Sources	Method of Preparation
Nitrogen	3.0	Air	Liquefaction of air
Phosphorus	2.1	Phosphate rock ($Ca_3(PO_4)_2$) Fluorapatite ($Ca_5(PO_4)_3F$)	$2Ca_3(PO_4)_2 + 6SiO_2 \rightarrow 6CaSiO_3 + P_4O_{10}$ $P_4O_{10} + 10C \rightarrow 4P + 10CO$
Arsenic	2.0	Arsenopyrite (Fe_3As_2 , FeS)	Heating arsenopyrite in the absence of air
Antimony	1.9	Stibnite (Sb_2S_3)	Roasting Sb_2S_3 in air to form Sb_2O_3 and then reduction with carbon
Bismuth	1.9	Bismite (Bi_2O_3), bismuth glance (Bi_2S_3)	Roasting Bi_2S_3 in air to form Bi_2O_3 and then reduction with carbon

**FIGURE 20.2**

The structures of the tetrahedral MX_4^+ and octahedral MX_6^- ions.

FIGURE 20.1

The molecules of the types MX_3 , MX_5 , and MX_6 formed by Group 5A elements.



known. Three pentahalides (BiF_5 , SbCl_5 , and SbF_5) are known, but these are molecular rather than ionic compounds.

The Group 5A elements can form molecules or ions that involve three, five, or six covalent bonds to the Group 5A atom. Examples involving three single bonds are NH_3 , PH_3 , NF_3 , and AsCl_3 . Each of these molecules has a lone pair of electrons (and thus can behave as a Lewis base) and a pyramidal shape as predicted by the VSEPR model (see Fig. 20.1).

All the Group 5A elements except nitrogen can form molecules with five covalent bonds (of general formula MX_5). Nitrogen cannot form such molecules because of its small size and lack of available d orbitals. The MX_5 molecules have a trigonal bipyramidal shape (see Fig. 20.1) as predicted by the VSEPR model, and the central atom is described as dsp^3 hybridized. The MX_5 molecules can accept an additional electron pair to form ionic species containing six covalent bonds. An example is



where the PF_6^- anion has an octahedral shape (see Fig. 20.1) and the phosphorus atom is described as d^2sp^3 hybridized.

Although the MX_5 molecules have a trigonal bipyramidal structure in the gas phase, the solids of many of these compounds contain the ions MX_4^+ and MX_6^-

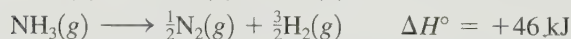
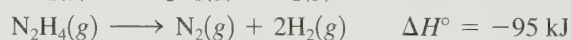
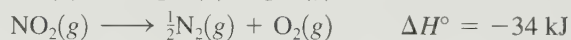
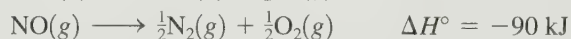
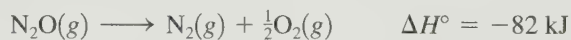
(Fig. 20.2), where the MX_4^+ cation is tetrahedral (the atom represented by M is described as sp^3 hybridized) and the MX_6^- anion is octahedral (the atom represented by M is described as d^2sp^3 hybridized). Examples are PCl_5 , which in the solid state contains PCl_4^+ and PCl_6^- , and AsF_3Cl_2 , which in the solid state contains AsCl_4^+ and AsF_6^- .

As discussed in Section 19.1, the ability of the Group 5A elements to form π bonds decreases dramatically after nitrogen. This explains why elemental nitrogen exists as N_2 molecules, whereas the other elements in the group exist as larger aggregates containing single bonds. For example, in the gas phase, the elements phosphorus, arsenic, and antimony consist of P_4 , As_4 , and Sb_4 molecules, respectively.

20.2 The Chemistry of Nitrogen

At the earth's surface, virtually all elemental nitrogen exists as the N_2 molecule with its very strong triple bond (941 kJ/mol). Because of this high bond strength, the N_2 molecule is so unreactive that it can coexist with most other elements under normal conditions without undergoing any appreciable reaction. This property makes nitrogen gas very useful as a medium for experiments involving substances that react with oxygen or water. Such experiments can be done using an inert-atmosphere box of the type shown in Fig. 20.3.

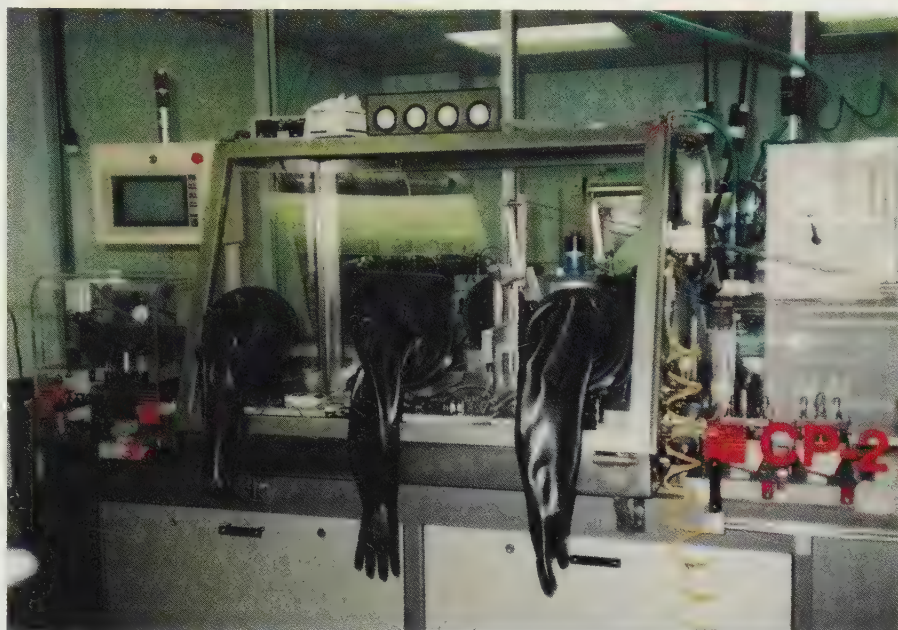
The strength of the triple bond in the N_2 molecule is important both thermodynamically and kinetically. Thermodynamically, the great stability of the $\text{N}\equiv\text{N}$ bond means that most binary compounds containing nitrogen decompose exothermically to the elements, for example:



At the Center for Disease Control in Atlanta, Georgia, a worker checks samples stored in a liquid nitrogen tank.

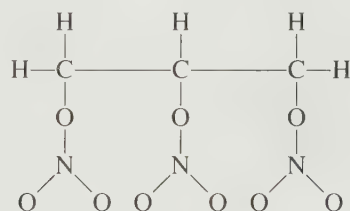
FIGURE 20.3

An inert-atmosphere box used when working with oxygen- or water-sensitive materials. The box is filled with an inert gas such as nitrogen, and work is done through the ports fitted with large rubber gloves.

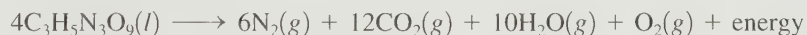


Of these compounds, only ammonia is thermodynamically more stable than its component elements. That is, only for ammonia is energy required (endothermic process, positive value of ΔH°) to decompose the molecule to its elements. For the remaining molecules, energy is released when decomposition to the elements occurs as a result of the great stability of N_2 .

The importance of the thermodynamic stability of N_2 can be seen clearly in the power of nitrogen-based explosives, such as nitroglycerin ($C_3H_5N_3O_9$), which has the structure

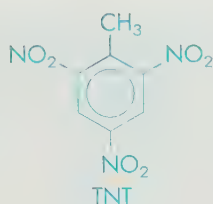


When ignited or subjected to sudden impact, nitroglycerin decomposes very rapidly and exothermically:



An explosion occurs; that is, large volumes of gas are produced in a fast, highly exothermic reaction. Note that 4 moles of liquid nitroglycerin produce 29 (6 + 12 + 10 + 1) moles of gaseous products. This alone produces a large increase in volume. However, also note that the products, including N_2 , are very stable molecules with strong bonds. Their formation is therefore accompanied by the release of large quantities of energy as heat, which increases the gaseous volume. The hot, rapidly expanding gases produce a pressure surge and damaging shock wave.

Pure nitroglycerin is quite dangerous because it explodes with little provocation. However, in 1867 the Swedish inventor Alfred Nobel found that if nitroglycerin is absorbed in porous silica, it can be handled quite safely. This tremendously



important explosive (see Fig. 20.4), which he called *dynamite*, earned Nobel a great fortune, which he subsequently used to establish the Nobel Prizes.

Most high explosives are organic compounds that, like nitroglycerin, contain nitro ($-\text{NO}_2$) groups and produce nitrogen and other gases as products. Another example is *trinitrotoluene*, or TNT, a solid at normal temperatures, which decomposes as follows:



Note that 2 moles of solid TNT produce 20 moles of gaseous products plus energy.

SAMPLE EXERCISE 20.1

Decomposition of NH_4NO_2

When ammonium nitrite is heated, it decomposes to nitrogen gas and water. Calculate the volume of N_2 gas produced from 1.00 g of solid NH_4NO_2 at 250°C and 1.00 atm.

SOLUTION

The decomposition reaction is



Using the molar mass of NH_4NO_2 (64.05 g/mol), we first calculate the moles of NH_4NO_2 :

$$1.00 \text{ g NH}_4\text{NO}_2 \times \frac{1 \text{ mol NH}_4\text{NO}_2}{64.05 \text{ g NH}_4\text{NO}_2} = 1.56 \times 10^{-2} \text{ mol NH}_4\text{NO}_2$$

Since 1 mol N_2 is produced for each mole of NH_4NO_2 , $1.56 \times 10^{-2} \text{ mol N}_2$ will be produced in the given experiment. We can calculate the volume of N_2 from the ideal gas law:

$$PV = nRT$$

In this case we have

$$P = 1.00 \text{ atm}$$

$$n = 1.56 \times 10^{-2} \text{ mol}$$

$$R = 0.08206 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol}$$

$$T = 250 + 273 = 523 \text{ K}$$

and the volume of N_2 is

$$\begin{aligned} V &= \frac{nRT}{P} = \frac{(1.56 \times 10^{-2} \text{ mol}) \left(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} \right) (523 \text{ K})}{1.00 \text{ atm}} \\ &= 0.670 \text{ L} \end{aligned}$$

See Exercises 20.17 and 20.18.



FIGURE 20.4
Chemical explosives are used to demolish a building in Miami, Florida.

The effect of bond strength on the kinetics of reactions involving the N_2 molecule is illustrated by the synthesis of ammonia from nitrogen and hydrogen, a reaction we have discussed many times before. Because a large quantity of energy is required to disrupt the $\text{N}\equiv\text{N}$ bond, the ammonia synthesis reaction has a negligible rate at room temperature, even though the equilibrium constant is very large

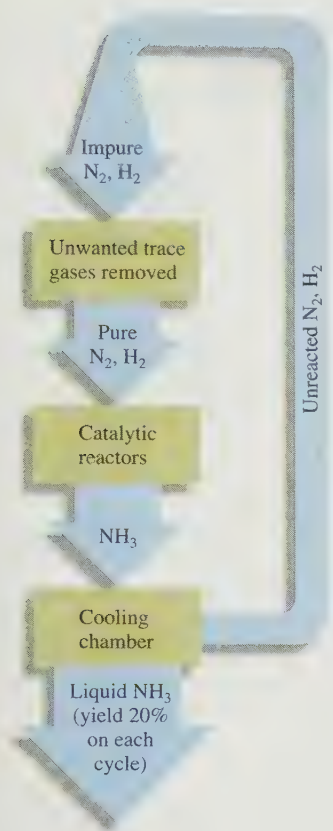


FIGURE 20.5

A schematic diagram of the Haber process for the manufacture of ammonia.



Nodules on the roots of pea plants contain nitrogen-fixing bacteria.

($K \approx 10^6$) at 25°C. Of course, the most direct way to increase the rate is to raise the temperature, but since the reaction is very exothermic, that is,



the value of K decreases significantly with a temperature increase (at 500°C, $K \approx 10^{-2}$).

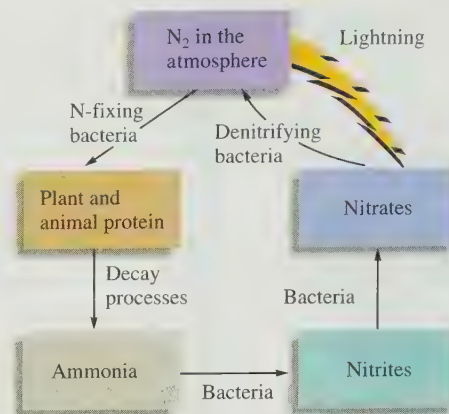
Obviously, the kinetics and the thermodynamics of this reaction are in opposition. A compromise must be reached: high pressure to force the equilibrium to the right and high temperature to produce a reasonable rate. The **Haber process** for manufacturing ammonia illustrates this compromise (see Fig. 20.5). The process is carried out at a pressure of about 250 atm and a temperature of approximately 400°C. Even higher temperatures would be required except that a catalyst, consisting of a solid iron oxide mixed with small amounts of potassium oxide and aluminum oxide, is used to facilitate the reaction.

Nitrogen is essential to living systems. The problem with nitrogen is not one of supply—we are surrounded by it—but of changing it from inert N_2 molecules to a form usable by plants and animals. The process of transforming N_2 to other nitrogen-containing compounds is called **nitrogen fixation**. The Haber process is one example of nitrogen fixation. The ammonia produced can be applied to the soil as a fertilizer, since plants can readily employ the nitrogen in ammonia to make the nitrogen-containing biomolecules essential for their growth.

Nitrogen fixation also results from the high-temperature combustion process in automobile engines. The nitrogen in the air drawn into the engine reacts at a significant rate with oxygen to form nitric oxide (NO), which further reacts with oxygen from the air to form nitrogen dioxide (NO_2). This nitrogen dioxide, which is an important contributor to photochemical smog in many urban areas (see Section 12.8), eventually reacts with moisture in the air and reaches the soil to form nitrate salts, which are plant nutrients.

Nitrogen fixation also occurs naturally. For example, lightning provides the energy to disrupt N_2 and O_2 molecules in the air, producing highly reactive nitrogen and oxygen atoms that attack other N_2 and O_2 molecules to form nitrogen oxides that eventually become nitrates. Although lightning traditionally has been credited with forming about 10% of the total fixed nitrogen, recent studies indicate that lightning may account for as much as half the fixed nitrogen available on earth. Another natural nitrogen fixation process is provided by bacteria that reside in the root nodules of plants such as beans, peas, and alfalfa. These **nitrogen-fixing bacteria** readily allow the conversion of nitrogen to ammonia and other nitrogen-containing compounds useful to plants. The efficiency of these bacteria is intriguing: They produce ammonia at soil temperature and 1 atm of pressure, whereas the Haber process requires severe conditions of 400°C and 250 atm. For obvious reasons, researchers are studying these bacteria intensively.

When plants and animals die, they decompose, and the elements they consist of are returned to the environment. In the case of nitrogen, the return of the element to the atmosphere as nitrogen gas, called **denitrification**, is carried out by bacteria that change nitrates to nitrogen. The complex **nitrogen cycle** is summarized in Fig. 20.6. It has been estimated that as much as 10 million tons per year more nitrogen is currently being fixed by natural and human processes than is being returned to the atmosphere. This fixed nitrogen is accumulating in the soil, lakes, rivers, and oceans, where it can promote the growth of algae and other undesirable organisms.

**FIGURE 20.6**

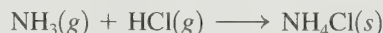
The nitrogen cycle. To be used by plants and animals, nitrogen must be converted from N_2 to nitrogen-containing compounds, such as nitrates, ammonia, and proteins. The nitrogen is returned to the atmosphere by natural decay processes.

Nitrogen Hydrides

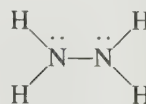
By far the most important hydride of nitrogen is **ammonia** (NH_3). A toxic, colorless gas with a pungent odor, ammonia is manufactured in huge quantities (~ 30 billion pounds per year), mainly for use in fertilizers.

The pyramidal ammonia molecule (see Fig. 20.1) has a lone pair of electrons on the nitrogen atom and polar N—H bonds. This structure leads to a high degree of intermolecular interaction by hydrogen bonding in the liquid state and produces an unusually high boiling point ($-33.4^\circ C$) for a substance of such low molar mass. Note, however, that the hydrogen bonding in liquid ammonia is clearly not as important as that in liquid water, which has about the same molar mass but a much higher boiling point. The water molecule has two polar bonds involving hydrogen and two lone pairs—the right combination for optimal hydrogen bonding—in contrast to the one lone pair and three polar bonds of the ammonia molecule.

As we saw in Chapter 14, ammonia behaves as a base and reacts with acids to produce ammonium salts, for example,

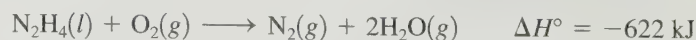


A second nitrogen hydride of major importance is **hydrazine** (N_2H_4). The Lewis structure of hydrazine is

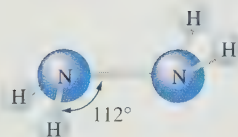


indicating that each nitrogen atom should be sp^3 hybridized with bond angles close to 109.5 degrees (the tetrahedral angle), since the nitrogen atom is surrounded by four electron pairs. The observed structure with bond angles of 112 degrees (see Fig. 20.7) agrees reasonably well with these predictions. Hydrazine, a colorless liquid with an ammonia-like odor, freezes at $2^\circ C$ and boils at $113.5^\circ C$. This boiling point is quite high for a compound with a molar mass of 32 g/mol; this suggests that considerable hydrogen bonding must occur among the polar hydrazine molecules.

Hydrazine is a powerful reducing agent that has been used widely as a rocket propellant. For example, its reaction with oxygen is highly exothermic:

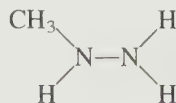


Since hydrazine also reacts vigorously with the halogens, fluorine is often used instead of oxygen as the oxidizer in rocket engines. Substituted hydrazines, where one

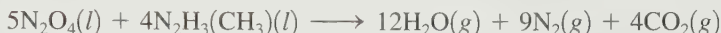
**FIGURE 20.7**

The molecular structure of hydrazine (N_2H_4). This arrangement minimizes the repulsion between the lone pairs on the nitrogen atoms by placing them on opposite sides.

or more of the hydrogen atoms are replaced by other groups, are also useful rocket fuels. For example, monomethylhydrazine,



is used with the oxidizer dinitrogen tetroxide (N_2O_4) to power the U.S. space shuttle orbiter. The reaction is



Because of the large number of gaseous molecules produced and the exothermic nature of this reaction, a very high thrust per mass of fuel is achieved. The reaction is also self-starting—it begins immediately when the fuels are mixed—which is a useful property for rocket engines that must be started and stopped frequently.

SAMPLE EXERCISE 20.2

Heats of Reaction from Bond Energies

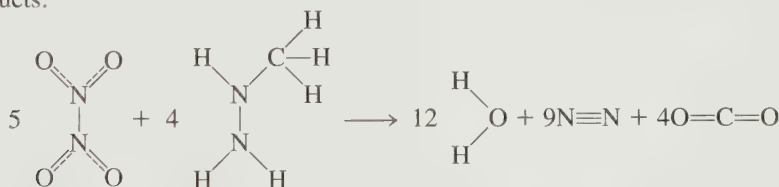
Using the bond energies in Table 8.4, calculate the approximate value of ΔH for the reaction between gaseous monomethylhydrazine and dinitrogen tetroxide:



The bonding in N_2O_4 is described by resonance structures that predict that the N—O bonds are intermediate in strength between single and double bonds (assume an average N—O bond energy of 440 kJ/mol).

SOLUTION

To calculate ΔH for this reaction, we must compare the energy necessary to break the bonds of the reactants and the energy released by formation of the bonds in the products:



Breaking bonds requires energy (positive sign), and forming bonds releases energy (negative sign). As summarized in the following table,

$$\Delta H = (21.1 \times 10^3 \text{ kJ}) - (26.1 \times 10^3 \text{ kJ}) = -5.0 \times 10^3 \text{ kJ}$$

The reaction is highly exothermic.

Bonds Broken	Energy Required (kJ/mol)	Bonds Formed	Energy Released (kJ/mol)
$5 \times 4 = 20 \text{ N}=\text{O}$	$20 \times 440 = 8.8 \times 10^3$	$12 \times 2 = 24 \text{ O}-\text{H}$	$24 \times 467 = 1.12 \times 10^4$
$5 + 4 = 9 \text{ N}-\text{N}$	$9 \times 160 = 1.4 \times 10^3$	$9 \text{ N}\equiv\text{N}$	$9 \times 941 = 8.5 \times 10^3$
$4 \times 3 = 12 \text{ N}-\text{H}$	$12 \times 391 = 4.7 \times 10^3$	$4 \times 2 = 8 \text{ C}=\text{O}$	$8 \times 799 = 6.4 \times 10^3$
$4 \times 3 = 12 \text{ C}-\text{H}$	$12 \times 413 = 5.0 \times 10^3$		
$4 \times 1 = 4 \text{ C}-\text{N}$	$4 \times 305 = 1.2 \times 10^3$		
Total	21.1×10^3	Total	26.1×10^3



Blowing agents such as hydrazine, which forms nitrogen gas on decomposition, are used to produce porous plastics like these styrofoam products.

The use of hydrazine as a rocket propellant is a rather specialized application. The main industrial use of hydrazine is as a “blowing” agent in the manufacture of plastics. Hydrazine decomposes to form nitrogen gas, which causes foaming in the liquid plastic, which results in a porous texture. Another major use of hydrazine is in the production of agricultural pesticides. Of the many hundreds of hydrazine derivatives (substituted hydrazines) that have been tested, 40 are used as fungicides, herbicides, insecticides, and plant growth regulators.

The manufacture of hydrazine involves the oxidation of ammonia by the hypochlorite ion in basic solution:



Although this reaction looks straightforward, the actual process involves many steps and requires high pressure, high temperature, and catalysis to optimize the yield of hydrazine in the face of many competing reactions.

Nitrogen Oxides

Nitrogen forms a series of oxides in which it has an oxidation state from +1 to +5, as shown in Table 20.2.

Dinitrogen monoxide (N_2O), more commonly called *nitrous oxide* or “laughing gas,” has an inebriating effect and has been used as a mild anesthetic by dentists.

TABLE 20.2 Some Common Nitrogen Compounds

Oxidation State of Nitrogen	Compound	Formula	Lewis Structure*
-3	Ammonia	NH_3	$\begin{array}{c} \text{H}-\ddot{\text{N}}-\text{H} \\ \\ \text{H} \end{array}$
-2	Hydrazine	N_2H_4	$\begin{array}{c} \text{H}-\ddot{\text{N}}-\ddot{\text{N}}-\text{H} \\ \quad \\ \text{H} \quad \text{H} \end{array}$
-1	Hydroxylamine	NH_2OH	$\begin{array}{c} \text{H}-\ddot{\text{N}}-\ddot{\text{O}}-\text{H} \\ \\ \text{H} \end{array}$
0	Nitrogen	N_2	$:\text{N}\equiv\text{N}:$
+1	Dinitrogen monoxide (nitrous oxide)	N_2O	$:\ddot{\text{N}}=\text{N}=\ddot{\text{O}}:$
+2	Nitrogen monoxide (nitric oxide)	NO	$:\ddot{\text{N}}=\ddot{\text{O}}:$
+3	Dinitrogen trioxide	N_2O_3	$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{O}-\text{N}-\text{N}=\text{O} \\ \diagdown \quad \diagup \\ \text{O} \end{array}$
+4	Nitrogen dioxide	NO_2	$:\ddot{\text{O}}-\ddot{\text{N}}=\ddot{\text{O}}:$
+5	Nitric acid	HNO_3	$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{O}-\text{N}-\text{O}-\text{H} \\ \diagdown \quad \diagup \\ \text{O} \end{array}$

* In some cases, additional resonance structures are needed to fully describe the electron distribution.

Because of its high solubility in fats, nitrous oxide is used widely as a propellant in aerosol cans of whipped cream. It is dissolved in the liquid in the can at high pressure and forms bubbles that produce foaming as the liquid is released from the can. A significant amount of N_2O exists in the atmosphere, mostly produced by soil microorganisms, and its concentration appears to be gradually increasing. Because it can strongly absorb infrared radiation, nitrous oxide plays a small but probably significant role in controlling the earth's temperature in the same way that atmospheric carbon dioxide and water vapor do (see the discussion of the greenhouse effect in Section 6.5). Some scientists fear that the rapid decrease of tropical rain forests resulting from development in countries such as Brazil will significantly affect the rate of production of N_2O by soil organisms and thus will have important effects on the earth's temperature.

In the laboratory, nitrous oxide is prepared by the thermal decomposition of ammonium nitrate:



Do not attempt this experiment unless you have the proper safety equipment.

This experiment must be done carefully because ammonium nitrate can explode. In fact, one of the greatest industrial disasters in U.S. history occurred in 1947 in Texas, when a ship loaded with ammonium nitrate for use as fertilizer exploded and killed nearly 600 people.

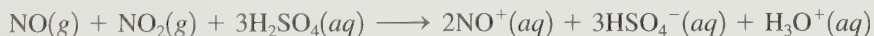
Nitrogen monoxide (NO), commonly called *nitric oxide*, is a colorless gas under normal conditions that can be produced in the laboratory by reaction of 6 *M* nitric acid with copper metal:



When this reaction is run in the air, the nitric oxide is immediately oxidized to brown nitrogen dioxide (NO_2).

Although nitric oxide is toxic when inhaled, it has been shown to be produced in certain tissues of the human body, where it behaves as a neurotransmitter. Current research indicates that nitric oxide plays a role in regulating blood pressure, blood clotting, and the muscle changes that allow erection of the penis in males.

Since the NO molecule has an odd number of electrons, it is most conveniently described in terms of the molecular orbital model. The molecular orbital energy-level diagram is shown in Fig. 20.8. Note that the NO molecule is paramagnetic and should have a bond order of 2.5, a prediction that is supported by experimental observations. Since the NO molecule has one high-energy electron, it is not surprising that it can be rather easily oxidized to form NO^+ , the *nitrosyl ion*. Because an antibonding electron is removed in going from NO to NO^+ , the ion should have a stronger bond (the predicted bond order is 3) than the molecule. This is borne out by experiment. The bond lengths and bond energies for nitric oxide and the nitrosyl ion are shown in Table 20.3. The nitrosyl ion is formed when nitric oxide and nitrogen dioxide are dissolved in concentrated sulfuric acid:



The ionic compound $\text{NO}^+\text{HSO}_4^-$ can be isolated from this solution.

Nitric oxide is thermodynamically unstable and decomposes to nitrous oxide and nitrogen dioxide:



A copper penny reacts with nitric acid to produce NO gas, which is immediately oxidized in air to brown NO_2 .

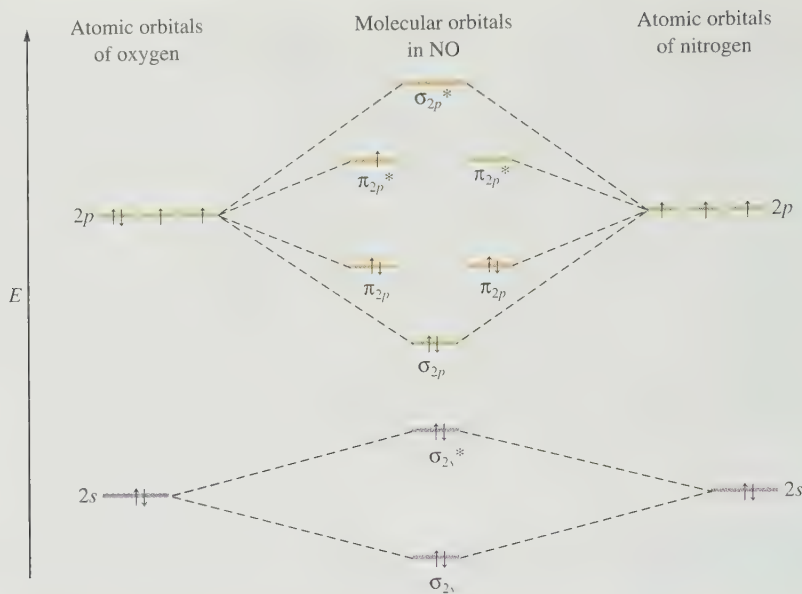


FIGURE 20.8
The molecular orbital energy-level diagram for nitric oxide (NO). The bond order is 2.5, or $(8 - 3)/2$.

TABLE 20.3 Comparison of the Bond Lengths and Bond Energies for Nitric Oxide and the Nitrosyl Ion

	NO	NO ⁺
Bond length (pm)	115	109
Bond energy (kJ/mol)	630	1020
Bond order (predicted by MO model)	2.5	3

Production of NO₂ by power plants and automobiles leads to smog (see Section 12.8).

Nitrogen dioxide (NO₂) is also an odd-electron molecule and has a V-shaped structure. The brown, paramagnetic NO₂ molecule readily dimerizes to form dinitrogen tetroxide,



which is diamagnetic and colorless. The value of the equilibrium constant is ~ 1 for this process at 55°C, and since the dimerization is exothermic, K decreases as the temperature increases.

SAMPLE EXERCISE 20.3

Molecular Orbital Description of NO[−]

Use the molecular orbital model to predict the bond order and magnetism of the NO[−] ion.

SOLUTION

Using the energy-level diagram for the NO molecule in Fig. 20.8, we can see that NO[−] has one more antibonding electron than NO. Thus there will be unpaired electrons in the two π_{2p}^* orbitals, and NO[−] will be paramagnetic with a bond order of $(8 - 4)/2$, or 2. Note that the bond in the NO[−] ion is weaker than that in the NO molecule.

See Exercises 20.23 and 20.24.

CHEMICAL IMPACT

Nitrous Oxide: Laughing Gas That Propels Whipped Cream and Cars

Nitrous oxide (N_2O), more properly called *dinitrogen monoxide*, is a compound with many interesting uses. It was discovered in 1772 by Joseph Priestly (who is also given credit for discovering oxygen gas), and its intoxicating effects were noted almost immediately. In 1798, the 20-year-old Humphry Davy became director of the Pneumatic Institute, which was set up to investigate the medical effects of various gases. Davy tested the effects of N_2O on himself, reporting that after inhaling 16 quarts of the gas in 7 minutes, he became “absolutely intoxicated.”

Over the next century “laughing gas,” as nitrous oxide became known, was developed as an anesthetic, particularly for dental procedures. Nitrous oxide is still used as an anesthetic, although it has been largely replaced by more modern drugs.

One major use of nitrous oxide today is as the propel-

lant in cans of “instant” whipped cream. The high solubility of N_2O in the whipped cream mixture makes it an excellent candidate for pressurizing the cans of whipped cream.

Another current use of nitrous oxide is to produce “instant horsepower” for hot rods and street racers. Because the reaction of N_2O with O_2 to form NO actually absorbs heat, this reaction has a cooling effect when placed in the fuel mixture in an automobile engine. This cooling effect lowers combustion temperatures, thus allowing the fuel–air mixture to be significantly more dense (the density of a gas is inversely proportional to temperature). This effect can produce a burst of additional power in excess of 200 horsepower. Because engines are not designed to run steadily at such high power levels, the nitrous oxide is injected from a tank when extra power is desired.

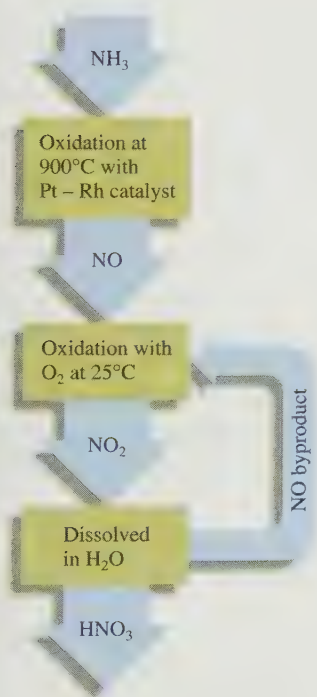
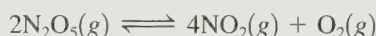


FIGURE 20.9
The Ostwald process.

The least common of the nitrogen oxides are *dinitrogen trioxide* (N_2O_3), a blue liquid that readily dissociates into gaseous nitric oxide and nitrogen dioxide, and *dinitrogen pentoxide* (N_2O_5), which under normal conditions is a solid that is best viewed as a mixture of NO_2^+ and NO_3^- ions. Although N_2O_5 molecules do exist in the gas phase, they readily dissociate to nitrogen dioxide and oxygen:

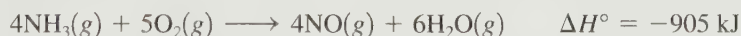


This reaction follows first-order kinetics, as was discussed in Section 12.4.

Oxyacids of Nitrogen

Nitric acid is an important industrial chemical (almost 10 million tons are produced annually) used in the manufacture of many products, such as nitrogen-based explosives and ammonium nitrate for use as fertilizer.

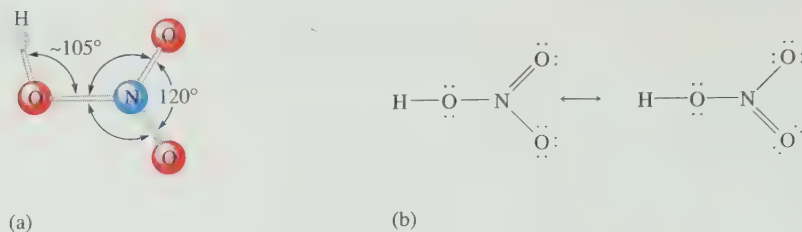
Nitric acid is produced commercially by the oxidation of ammonia in the **Ostwald process** (see Fig. 20.9). In the first step of this process, ammonia is oxidized to nitric oxide:



Although this reaction is highly exothermic, it is very slow at 25°C. There is also a side reaction between nitric oxide and ammonia:



which is particularly undesirable because it traps the nitrogen as very unreactive N_2 molecules. To speed up the desired reaction and minimize the effects of the competing reaction, the ammonia oxidation is carried out using a catalyst of a platinum–rhodium alloy heated to 900°C. Under these conditions, there is a 97% conversion of the ammonia to nitric oxide.

**FIGURE 20.10**

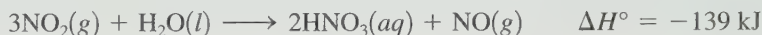
(a) The molecular structure of HNO₃. (b) The resonance structures of HNO₃.

In the second step, nitric oxide reacts with oxygen to produce nitrogen dioxide:



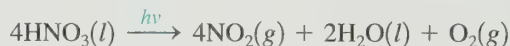
This oxidation reaction has a rate that *decreases* with increasing temperature. Because of this very unusual behavior, the reaction is carried out at $\sim 25^\circ\text{C}$ and is kept at this temperature by cooling with water.

The third step in the Ostwald process is the absorption of nitrogen dioxide by water:



The gaseous NO produced in this reaction is recycled to be oxidized to NO₂. The aqueous nitric acid from this process is about 50% HNO₃ by mass, which can be increased to 68% by distillation to remove some of the water. The maximum concentration attainable this way is 68% because nitric acid and water form an *azeotrope* at this concentration. The solution can be further concentrated to 95% HNO₃ by treatment with concentrated sulfuric acid, which strongly absorbs water; H₂SO₄ is often used as a dehydrating (water-removing) agent.

Nitric acid is a colorless, fuming liquid (bp = 83°C) with a pungent odor; it decomposes in sunlight via the following reaction:



As a result, nitric acid turns yellow as it ages because of the dissolved nitrogen dioxide. The common laboratory reagent known as concentrated nitric acid is 15.9 M HNO₃ (70.4% HNO₃ by mass) and is a very strong oxidizing agent. The resonance structures and molecular structure of HNO₃ are shown in Fig. 20.10. Note that the hydrogen is bound to an oxygen atom rather than to nitrogen, as the formula suggests.

Nitric acid reacts with metal oxides, hydroxides, and carbonates and with other ionic compounds containing basic anions to form nitrate salts. For example,

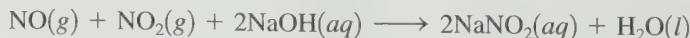


Nitrate salts are generally very soluble in water.

Nitrous acid (HNO₂) is a weak acid,



that forms pale yellow nitrite (NO₂[−]) salts. In contrast to nitrates, which are often used as explosives, nitrites are quite stable even at high temperatures. Nitrites are usually prepared by bubbling equal numbers of moles of nitric oxide and nitrogen dioxide into the appropriate aqueous solution of a metal hydroxide, for example,



An *azeotrope* is a solution that, like a pure liquid, distills at a constant temperature without a change in composition.

20.3 The Chemistry of Phosphorus

Although phosphorus lies directly below nitrogen in Group 5A of the periodic table, its chemical properties are significantly different from those of nitrogen. The differences arise mainly from four factors: nitrogen's ability to form much stronger π bonds, the greater electronegativity of nitrogen, the larger size of the phosphorus atom, and the availability of empty valence d orbitals on phosphorus.

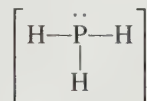
The chemical differences are apparent in the elemental forms of nitrogen and phosphorus. In contrast to the diatomic form of elemental nitrogen, which is stabilized by strong π bonds, there are several solid forms of phosphorus, all containing aggregates of atoms. *White phosphorus*, which contains discrete tetrahedral P_4 molecules [see Fig. 20.11(a)], is very reactive and bursts into flames on contact with air (it is said to be *pyrophoric*). To prevent this, white phosphorus is commonly stored under water. White phosphorus is quite toxic, and the P_4 molecules are very damaging to tissue, particularly the cartilage and bones of the nose and jaw. The much less reactive forms known as *black phosphorus* and *red phosphorus* are network solids (see Section 10.5). Black phosphorus has a regular crystalline structure [Fig. 20.11(b)], but red phosphorus is amorphous and is thought to consist of chains of P_4 units [Fig. 20.11(c)]. Red phosphorus can be obtained by heating white phosphorus in the absence of oxygen at 1 atm. Black phosphorus is obtained from either white or red phosphorus by heating at high pressures.

Even though phosphorus has a lower electronegativity than nitrogen, it will form phosphides (ionic substances containing the P^{3-} anion) such as Na_3P and Ca_3P_2 . Phosphide salts react vigorously with water to produce *phosphine* (PH_3), a toxic, colorless gas:



Phosphine is analogous to ammonia, although it is a much weaker base ($K_b \approx 10^{-26}$) and much less soluble in water. Because phosphine has a relatively small affinity for protons, phosphonium (PH_4^+) salts are very uncommon and not very stable—only PH_4I , PH_4Cl , and PH_4Br are known.

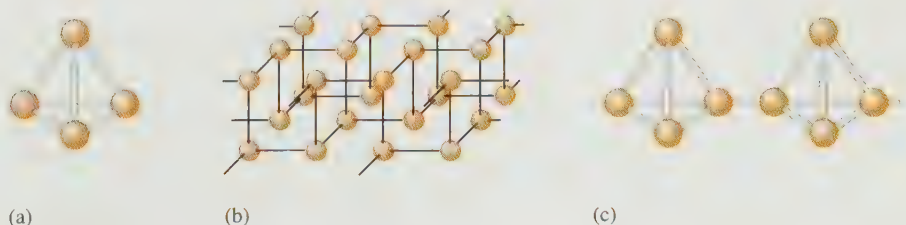
Phosphine has the Lewis structure



and a pyramidal molecular structure, as we would predict from the VSEPR model. However, it has bond angles of 94 degrees, rather than 107 degrees, as found in the ammonia molecule. The reasons for this are complex, and we will simply regard phosphine as an exception to the simple version of the VSEPR model that we use.

FIGURE 20.11

(a) The P_4 molecule found in white phosphorus. (b) The crystalline network structure of black phosphorus. (c) The chain structure of red phosphorus.



CHEMICAL IMPACT

Phosphorus: An Illuminating Element

The elemental form of phosphorus was discovered by accident in 1669 by German alchemist Henning Brand when he heated dried urine with sand (alchemists often investigated the chemistry of body fluids in an attempt to better understand the “stuff of life”). When Brand passed the resulting vapors through water, he was able to isolate the form of elemental phosphorus known as *white phosphorus* (contains P_4 molecules). The name *phosphorus* is derived from the Latin *phos*, meaning “light,” and *phorus*, meaning “bearing.” It seems that when Brand stored the solid white phosphorus in a sealed bottle, it glowed in the dark! This effect—a glow that persists even after the light source has been removed—came to be called *phosphorescence*. Interestingly, the term phosphorescence is derived from the name of an element that really does not phosphoresce. The glow that Brand saw actually was the result of a reaction of oxygen from the air on the surface of white phosphorus. If isolated completely from air, phosphorus does not glow in the dark after being irradiated.

After its discovery, phosphorus became quite a novelty in the seventeenth century. People would deposit a film of phosphorus on their faces and hands so that they would glow in the dark.* This fascination was short-lived—painful, slow-healing burns result from the spontaneous reaction of phosphorus with oxygen from the air.

The greatest consumer use of phosphorus compounds concerns the chemistry of matches. Two kinds of matches are currently available—strike-anywhere matches and safety matches. Both types of matches use phosphorus (in different forms) to help initiate a flame at the match head. The chemistry of matches is quite interesting. The tip of a strike-anywhere match is made from a mixture of powdered glass,

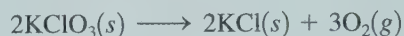


The phosphorus in safety matches helps ignite the flame in the match.

binder, and tetraphosphorus trisulfide (P_4S_3). When the match is struck, friction ignites the combustion reaction of P_4S_3 :

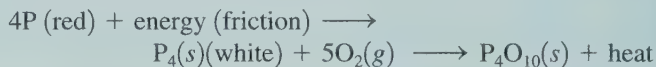


The heat from this reaction causes an oxidizing agent such as potassium chlorate to decompose:



which in turn causes solid sulfur to melt and react with oxygen, producing sulfur dioxide and more heat. This then ignites a paraffin wax that helps to “light” the wooden stem of the match.

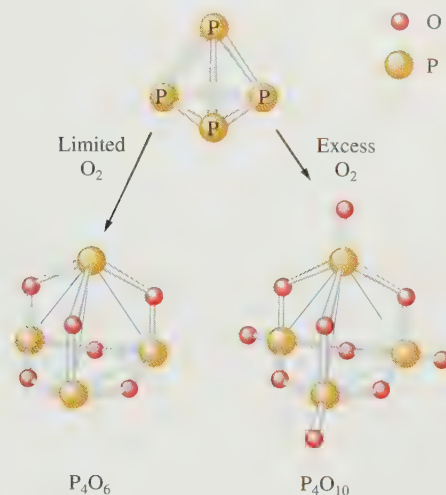
The chemistry of a safety match is quite similar, but the location of the reactants is different. The phosphorus needed to initiate all the reactions is found on the striking surface of the box. Thus, in theory, a safety match is able to ignite only when used with the box. For a safety match, the striking surface contains red phosphorus, which is easily converted to white phosphorus by the friction of the match head on the striking surface. White phosphorus ignites spontaneously in air and generates enough heat to initiate all the other reactions to ignite the match stem.



*An interesting reference to white phosphorus can be found in the Sherlock Holmes mystery, *The Hound of the Baskervilles*, where a large dog was coated with white phosphorus to scare Baskerville family members to death.

Phosphorus Oxides and Oxyacids

Phosphorus reacts with oxygen to form oxides in which it has oxidation states of +5 and +3. The oxide P_4O_6 is formed when elemental phosphorus is burned in a limited supply of oxygen, and P_4O_{10} is produced when the oxygen is in excess. These oxides, as shown in Fig. 20.12, can be pictured as being constructed by adding oxygen atoms to the fundamental P_4 structure. The intermediate states, P_4O_7 , P_4O_8 , and

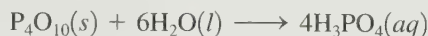
**FIGURE 20.12**The structures of P_4O_6 and P_4O_{10} .

The terminal oxygens are the nonbridging oxygen atoms.

P_4O_9 , which contain one, two, and three terminal oxygen atoms, respectively, are also known.

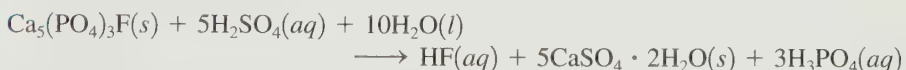
Tetraphosphorus decoxide (P_4O_{10}), which was formerly represented as P_2O_5 , has a great affinity for water and thus is a powerful dehydrating agent. For example, it can be used to convert HNO_3 and H_2SO_4 to their parent oxides, N_2O_5 and SO_3 , respectively.

When tetraphosphorus decoxide dissolves in water, **phosphoric acid** (H_3PO_4), also called **orthophosphoric acid**, is produced:



Pure phosphoric acid is a white solid that melts at 42°C . Aqueous phosphoric acid is a much weaker acid ($K_{a1} \approx 10^{-2}$) than nitric acid or sulfuric acid and is a poor oxidizing agent.

Phosphate minerals are the main source of phosphoric acid. Unlike nitrogen, phosphorus is found in nature exclusively in a combined state, principally as the PO_4^{3-} ion in phosphate rock, which is mainly calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$, and fluorapatite, $\text{Ca}_5(\text{PO}_4)_3\text{F}$. Fluorapatite can be converted to phosphoric acid by grinding up the phosphate rock and forming a slurry with sulfuric acid:



(A similar reaction can be written for the conversion of calcium phosphate.) The solid product $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, called *gypsum*, is used to manufacture wallboard for the construction of buildings.

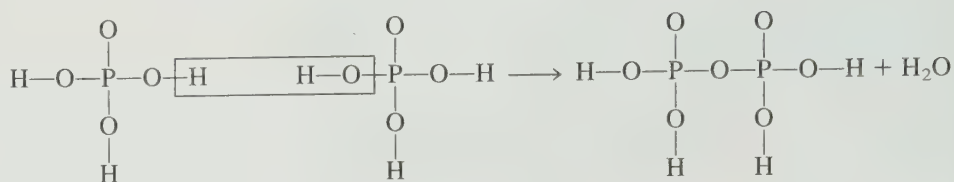
The process just described, called the *wet process*, produces only impure phosphoric acid. In another procedure, phosphate rock, sand (SiO_2), and coke are heated in an electric furnace to form white phosphorus:



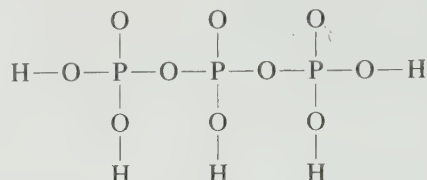
The white phosphorus obtained is burned in air to form tetraphosphorus decoxide, which is then combined with water to give phosphoric acid.

Phosphoric acid easily undergoes **condensation reactions**, where a molecule of water is eliminated in the joining of two molecules of acid:

The mineral hydroxyapatite, $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, the principal component of tooth enamel, can be converted to fluorapatite by reaction with fluoride. Fluoride ions added to drinking water and toothpaste help prevent tooth decay because fluorapatite is less soluble in the acids of the mouth than hydroxyapatite.



The product ($\text{H}_4\text{P}_2\text{O}_7$) is called *pyrophosphoric acid*. Further heating produces polymers, such as *tripolyphosphoric acid* ($\text{H}_5\text{P}_3\text{O}_{10}$), which has the structure



The sodium salt of tripolyphosphoric acid is widely used in detergents because the $\text{P}_3\text{O}_{10}^{5-}$ anion can form complexes with metal ions such as Mg^{2+} and Ca^{2+} , which would otherwise interfere with detergent action.

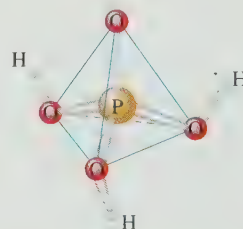
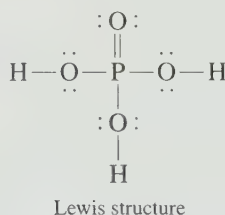
SAMPLE EXERCISE 20.4

Structure of Phosphoric Acid

What are the molecular structure and the hybridization of the central atom of the phosphoric acid molecule?

SOLUTION

In the phosphoric acid molecule, the hydrogen atoms are attached to oxygens, and the Lewis structure is as shown below. Thus the phosphorus atom is surrounded by four effective pairs, which are arranged tetrahedrally. The atom is described as sp^3 hybridized.



See Exercises 20.27 and 20.28.

When P_4O_6 is placed in water, **phosphorous acid** (H_3PO_3) is formed [Fig. 20.13(a)]. Although the formula suggests a triprotic acid, phosphorous acid is

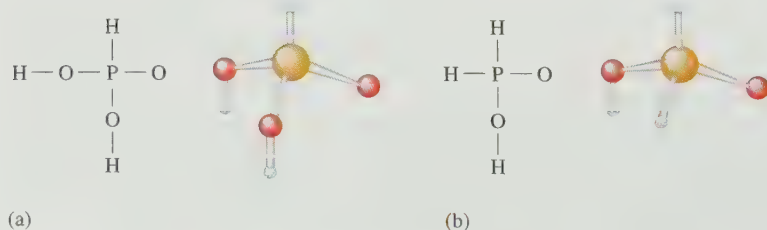
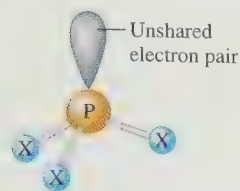
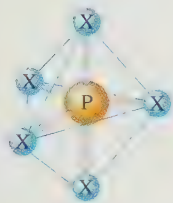


FIGURE 20.13

(a) The structure of phosphorous acid (H_3PO_3). (b) The structure of hypophosphorous acid (H_3PO_2).



(a)



(b)

FIGURE 20.14

Structures of the phosphorus halides. (a) The PX_3 compounds have pyramidal molecules. (b) The gaseous and liquid phases of the PX_5 compounds are composed of trigonal bipyramidal molecules.

a *diprotic* acid. The hydrogen atom bonded directly to the phosphorus atom is not acidic in aqueous solution; only those hydrogen atoms bonded to the oxygen atoms in H_3PO_3 can be released as protons.

A third oxyacid of phosphorus is *hypophosphorous acid* (H_3PO_2) [Fig. 20.13(b)], which is a monoprotic acid.

Phosphorus in Fertilizers

Phosphorus is essential for plant growth. Although most soil contains large amounts of phosphorus, it is often present as insoluble minerals, which makes it inaccessible to plants. Soluble phosphate fertilizers are manufactured by treating phosphate rock with sulfuric acid to make **superphosphate of lime**, a mixture of $CaSO_4 \cdot 2H_2O$ and $Ca(H_2PO_4)_2 \cdot H_2O$. If phosphate rock is treated with phosphoric acid, $Ca(H_2PO_4)_2$, or *triple phosphate*, is produced. The reaction of ammonia and phosphoric acid gives *ammonium dihydrogen phosphate* ($NH_4H_2PO_4$), a very efficient fertilizer because it furnishes both phosphorus and nitrogen.

Phosphorus Halides

Phosphorus forms all possible halides of the general formulas PX_3 and PX_5 , with the exception of PI_5 . The PX_3 molecule has the expected pyramidal structure [Fig. 20.14(a)]. Under normal conditions of temperature and pressure, PF_3 is a colorless gas, PCl_3 is a liquid (bp = 74°C), PBr_3 is a liquid (bp = 175°C), and PI_3 is an unstable red solid (mp = 61°C). All the PX_3 compounds react with water to produce phosphorous acid:



In the gaseous and liquid states, the PX_5 compounds have molecules with a trigonal bipyramidal structure [Fig. 20.14(b)]. However, PCl_5 and PBr_5 form ionic solids: Solid PCl_5 contains a mixture of octahedral PCl_6^- ions and tetrahedral PCl_4^+ ions, and solid PBr_5 appears to consist of PBr_4^+ and Br^- ions.

The PX_5 compounds react with water to form phosphoric acid:



20.4 The Group 6A Elements

6A
O
S
Se
Te
Po

Although in Group 6A (Table 20.4) there is the usual tendency for metallic properties to increase going down the group, none of the Group 6A elements (valence-electron configuration n^2np^4) behaves as a typical metal. The most common chemical behavior of a Group 6A atom is to achieve a noble gas electron configuration by adding two electrons to become a $2-$ anion in ionic compounds with metals. In fact, for most metals, the oxides and sulfides constitute the most common minerals.

The Group 6A elements can form covalent bonds with other nonmetals. For example, they combine with hydrogen to form a series of covalent hydrides of the general formula H_2X . Those members of the group that have valence d orbitals available (all except oxygen) commonly form molecules in which they are surrounded by more than eight electrons. Examples are SF_4 , SF_6 , TeI_4 , and $SeBr_4$.

In recent years there has been a growing interest in the chemistry of selenium, an element found throughout the environment in trace amounts. Selenium's toxicity

TABLE 20.4 Selected Physical Properties, Sources, and Methods of Preparation for the Group 6A Elements

Element	Electro-negativity	Radius of X^{2-} (pm)	Source	Method of Preparation
Oxygen	3.5	140	Air	Distillation from liquid air
Sulfur	2.5	184	Sulfur deposits	Melted with hot water and pumped to the surface
Selenium	2.4	198	Impurity in sulfide ores	Reduction of H_2SeO_4 with SO_2
Tellurium	2.1	221	Nagyagite (mixed sulfide and telluride)	Reduction of ore with SO_2
Polonium	2.0	230	Pitchblende	

has long been known, but recent medical studies have shown an *inverse* relationship between the incidence of cancer and the selenium levels in soil. It has been suggested that the resulting greater dietary intake of selenium by people living in areas of relatively high levels of selenium somehow furnishes protection from cancer. These studies are only preliminary, but selenium is known to be physiologically important (it is involved in the activity of vitamin E and certain enzymes) and selenium deficiency has been shown to be connected to the occurrence of congestive heart failure. Also of importance is the fact that selenium (along with tellurium) is a semiconductor and therefore finds some application in the electronics industry.

Polonium was discovered in 1898 by Marie and Pierre Curie in their search for the sources of radioactivity in pitchblende. Polonium has 27 isotopes and is highly toxic and very radioactive. It has been suggested that the isotope ^{210}Po , a natural contaminant of tobacco and an α -particle emitter (see Section 18.1), might be at least partly responsible for the incidence of cancer in smokers.

20.5 The Chemistry of Oxygen

It is hard to overstate the importance of oxygen, the most abundant element in and near the earth's crust. Oxygen is present in the atmosphere in oxygen gas and ozone; in soil and rocks in oxide, silicate, and carbonate minerals; in the oceans in water; and in our bodies in water and in a myriad of molecules. In addition, most of the energy we need to live and to run our civilization comes from the exothermic reactions of oxygen and carbon-containing molecules.

The most common elemental form of oxygen (O_2) constitutes 21% of the volume of the earth's atmosphere. Since nitrogen has a lower boiling point than oxygen, nitrogen can be boiled away from liquid air, leaving oxygen and small amounts of argon, another component of air. Liquid oxygen is a pale blue liquid that freezes at -219°C and boils at -183°C . The paramagnetism of the O_2 molecule can be demonstrated by pouring liquid oxygen between the poles of a strong magnet, where it "sticks" as it boils away (see Fig. 9.40). The paramagnetism of the O_2 molecule can be accounted for by the molecular orbital model (see Fig. 9.39), which also explains its bond strength.

The other form of elemental oxygen is **ozone** (O_3), a molecule that can be represented by the resonance structures



The bond angle in the O_3 molecule is 117 degrees, in reasonable agreement with the prediction of the VSEPR model (three effective pairs require a trigonal planar arrangement). That the bond angle is slightly less than 120 degrees can be explained by concluding that more space is required for the lone pair than for the bonding pairs.

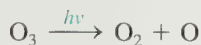
Ozone can be prepared by passing an electric discharge through pure oxygen gas. The electrical energy disrupts the bonds in some O_2 molecules to give oxygen atoms, which react with other O_2 molecules to form O_3 . Ozone is much less stable than oxygen at 25°C and 1 atm. For example, $K \approx 10^{-57}$ for the equilibrium



A pale blue, highly toxic gas, ozone is a much more powerful oxidizing agent than oxygen. Because of its oxidizing ability, ozone is being considered as a replacement for chlorine in municipal water purification. Chlorine leaves residues of chloro compounds, such as chloroform (CHCl_3), which may cause cancer after long-term exposure. Although ozone effectively kills the bacteria in water, one problem with **ozonolysis** is that the water supply is not protected against recontamination, since virtually no ozone remains after the initial treatment. In contrast, for chlorination, significant residual chlorine remains after treatment.

The oxidizing ability of ozone can be highly detrimental, especially when it is formed in the pollution from automobile exhausts (see Section 5.9).

Ozone exists naturally in the upper atmosphere of the earth. The *ozone layer* is especially important because it absorbs ultraviolet light and thus acts as a screen to prevent this radiation, which can cause skin cancer, from penetrating to the earth's surface. When an ozone molecule absorbs this energy, it splits into an oxygen molecule and an oxygen atom:

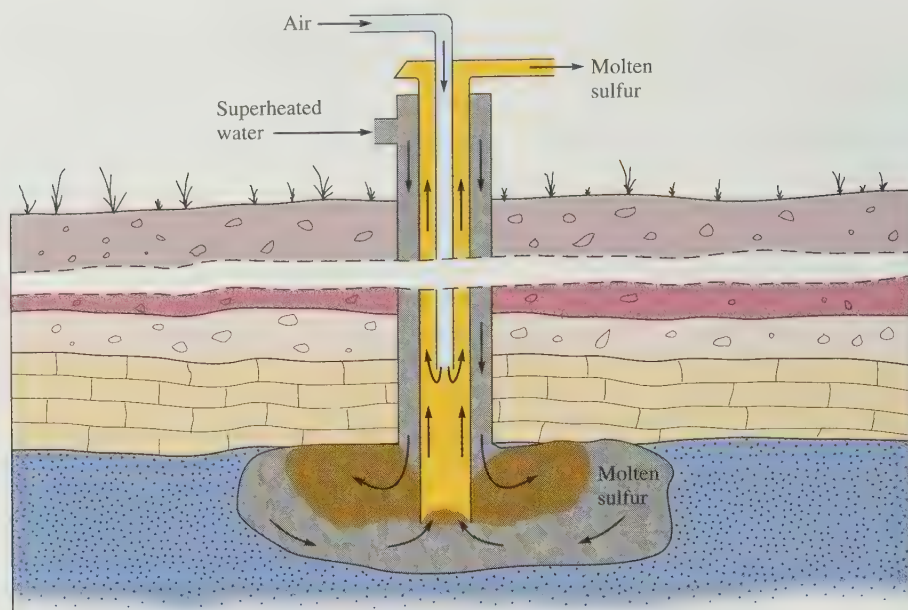


If the oxygen molecule and atom collide, they will not stay together as ozone unless a “third body,” such as a nitrogen molecule, is present to help absorb the energy released in the bond formation. The third body absorbs the energy as kinetic energy; its temperature is increased. Therefore, the energy originally absorbed as ultraviolet radiation is eventually changed to thermal energy. Thus the ozone prevents the harmful high-energy ultraviolet light from reaching the earth.

20.6 The Chemistry of Sulfur

Sulfur is found in nature both in large deposits of the free element and in widely distributed ores, such as galena (PbS), cinnabar (HgS), pyrite (FeS_2), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), and glauberite ($\text{Na}_2\text{SO}_4 \cdot \text{CaSO}_4$).

About 60% of the sulfur produced in the United States comes from the underground deposits of elemental sulfur found in Texas and Louisiana. This sulfur is recovered using the **Frasch process** developed by Herman Frasch in the 1890s. Superheated water is pumped into the deposit to melt the sulfur ($\text{mp} = 113^\circ\text{C}$),

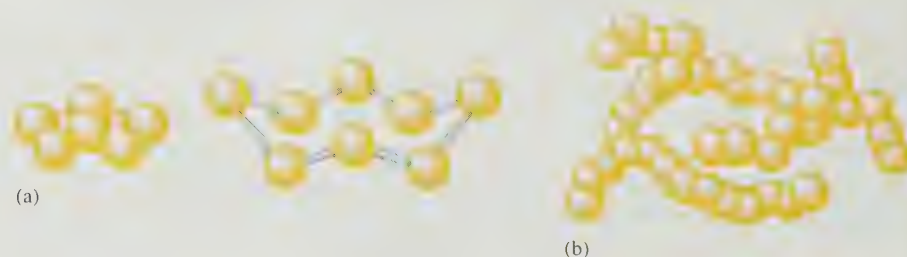
**FIGURE 20.15**

The Frasch process for recovering sulfur from underground deposits.

which is then forced to the surface by air pressure (see Fig. 20.15). The remaining 40% of sulfur produced in the United States is either a by-product of the purification of fossil fuels before combustion to prevent pollution or from the sulfur dioxide (SO_2) scrubbed from the exhaust gases when sulfur-containing fuels are burned.

In contrast to oxygen, elemental sulfur exists as S_2 molecules only in the gas phase at high temperatures. Because sulfur atoms form much stronger σ bonds than π bonds, S_2 is less stable at 25°C than larger aggregates such as S_6 and S_8 rings and S_n chains (Fig. 20.16). The most stable form of sulfur at 25°C and 1 atm is called *rhombic sulfur* [see Fig. 20.17(a)], which contains stacked S_8 rings. If rhombic sulfur is melted and heated to 120°C , it forms *monoclinic sulfur* as it cools slowly [Fig. 20.17(b)]. This form also contains S_8 rings, but the rings are stacked differently than they are in rhombic sulfur.

As sulfur is heated beyond its melting point, a relatively nonviscous liquid containing S_8 rings forms initially. With continued heating, the liquid becomes highly viscous as the rings first break and then link up to form long chains. Further heating lowers the viscosity because the long chains are broken down as the energetic sulfur atoms break loose. If the liquid is suddenly cooled, a substance called *plastic sulfur*, which contains S_n chains and has rubberlike qualities, is formed. Eventually, this form reverts back to the more stable S_8 rings.

**FIGURE 20.16**

(a) The S_8 molecule. (b) Chains of sulfur atoms in viscous liquid sulfur. The chains may contain as many as 10,000 atoms.



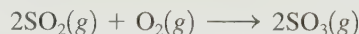
Pouring liquid sulfur into water to produce plastic sulfur.

Sulfur Oxides

From its position below oxygen in the periodic table, we might expect the simplest stable oxide of sulfur to have the formula SO . However, *sulfur monoxide*, which can be produced in small amounts when gaseous sulfur dioxide (SO_2) is subjected to an electrical discharge, is very unstable. The difference in the stabilities of the O_2 and SO molecules probably reflects the stronger π bonding between oxygen atoms than between sulfur and oxygen atoms.

Sulfur burns in air with a bright blue flame to give *sulfur dioxide* (SO_2), a colorless gas with a pungent odor, which condenses to a liquid at -10°C and 1 atm. Sulfur dioxide is a very effective antibacterial agent and is often used to preserve stored fruit. Its structure is given in Fig. 20.18.

Sulfur dioxide reacts with oxygen to produce *sulfur trioxide* (SO_3):



However, this reaction is very slow in the absence of a catalyst. One of the mysteries during early research on air pollution was how the sulfur dioxide produced from the combustion of sulfur-containing fuels is so rapidly converted to sulfur trioxide. It is now known that dust and other particles can act as heterogeneous catalysts for this process (see Section 12.8). In the preparation of sulfur trioxide for the manufacture of sulfuric acid, a platinum or vanadium(V) oxide (V_2O_5) catalyst is used, and the reaction is carried out at $\sim 500^\circ\text{C}$, even though this temperature decreases the value of the equilibrium constant for this exothermic reaction.

The bonding in the SO_3 molecule is usually described in terms of the resonance structures shown in Fig. 20.19. The molecule is trigonal planar, as predicted by the VSEPR model. Sulfur trioxide is a corrosive gas with a choking odor that forms white fumes of sulfuric acid when it reacts with moisture in the air. Thus sulfur trioxide and nitrogen dioxide, which reacts with water to form a mixture of nitrous and nitric acids, are the major culprits in the formation of acid rain.

Sulfur trioxide condenses to a colorless liquid at 44.5°C and freezes at 16.8°C to give three solid forms, one containing S_3O_9 rings and the other two containing $(\text{SO}_3)_x$ chains (Fig. 20.20).



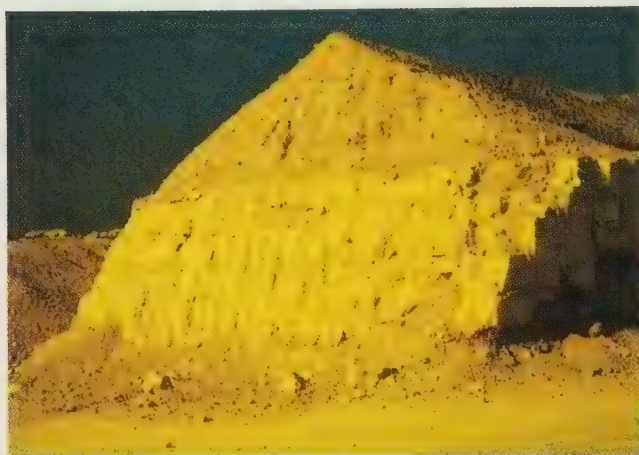
(a)



(b)

FIGURE 20.17

(a) Crystals of rhombic sulfur. (b) Crystals of monoclinic sulfur.



(left) A sulfur deposit. (right) Melted sulfur obtained from underground deposits by the Frasch process.

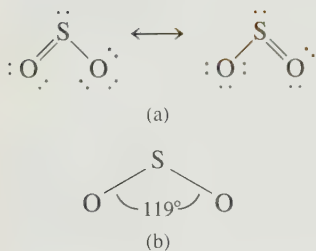
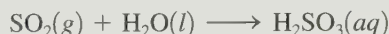


FIGURE 20.18

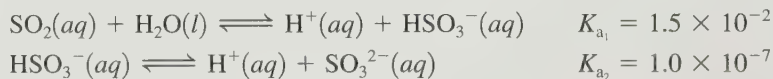
(a) Two of the resonance structures for SO_2 . (b) SO_2 is a bent molecule with a 119-degree bond angle, as predicted by the VSEPR model.

Oxyacids of Sulfur

Sulfur dioxide dissolves in water to form an acidic solution. The reaction is often represented as

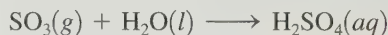


where H_2SO_3 is called *sulfurous acid*. However, very little H_2SO_3 actually exists in the solution. The major form of sulfur dioxide in water is SO_2 , and the acid dissociation equilibria are best represented as



This situation is analogous to the behavior of carbon dioxide in water (see Section 14.7). Although H_2SO_3 cannot be isolated, salts of SO_3^{2-} (*sulfites*) and HSO_3^- (*hydrogen sulfites*) are well known.

Sulfur trioxide reacts violently with water to produce the diprotic acid **sulfuric acid**:



Manufactured in greater amounts than any other chemical, sulfuric acid is usually produced by the *contact process*, which is described at the end of Chapter 3. About 60% of the sulfuric acid manufactured in the United States is used to produce fertilizers from phosphate rock (see Section 20.3). The other 40% is used in lead

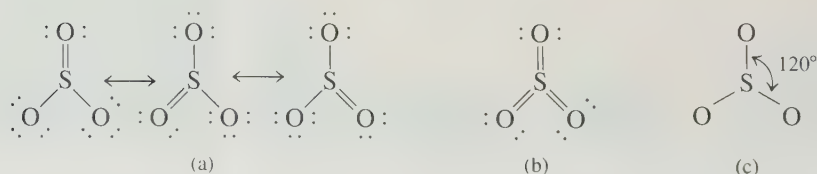
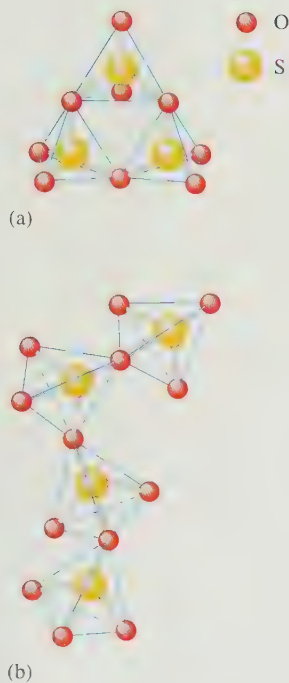


FIGURE 20.19

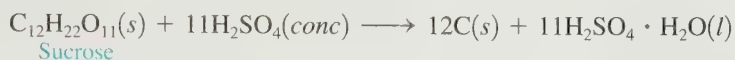
(a) Three of the resonance structures of SO_3 . (b) A resonance structure with three double bonds. (c) SO_3 is a planar molecule with 120-degree bond angles.

**FIGURE 20.20**

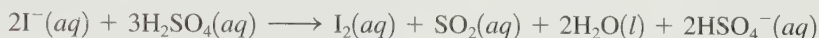
Different structures for solid SO_3 . (a) S_3O_9 rings. (b) $(\text{SO}_3)_x$ chains. In both cases the sulfur atoms are surrounded by a tetrahedral arrangement of oxygen atoms.

storage batteries and in petroleum refining, in steel manufacturing, and for various purposes in most of the chemical industries.

Because sulfuric acid has a high affinity for water, it is often used as a dehydrating agent. Gases that do not react with sulfuric acid, such as oxygen, nitrogen, and carbon dioxide, are often dried by bubbling them through concentrated solutions of the acid. Sulfuric acid is such a powerful dehydrating agent that it will remove hydrogen and oxygen from a substance in a 2:1 ratio even when the substance contains no molecular water. For example, concentrated sulfuric acid reacts vigorously with common table sugar (sucrose), leaving a charred mass of carbon (see Fig. 20.21):



Sulfuric acid is a moderately strong oxidizing agent, especially at high temperatures. Hot concentrated sulfuric acid oxidizes bromide or iodide ions to elemental bromine or iodine, for example,



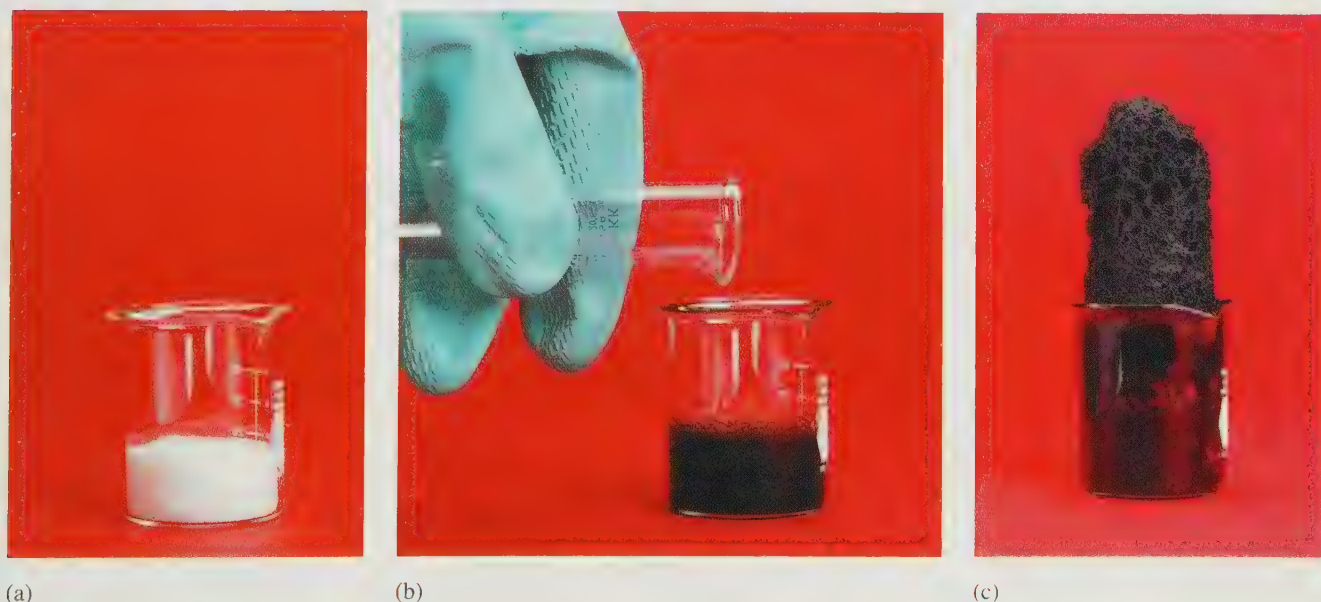
Hot sulfuric acid attacks copper metal:



The cold acid does not react with copper.

Other Compounds of Sulfur

Sulfur reacts with both metals and nonmetals to form a wide variety of compounds in which it has a +6, +4, +2, 0, or -2 oxidation state (see Table 20.5). The -2

**FIGURE 20.21**

(a) A beaker of sucrose (table sugar). (b) Concentrated sulfuric acid reacts with the sucrose to produce a column of carbon (c), accompanied by an intense burnt-sugar odor.

TABLE 20.5 Common Compounds of Sulfur with Various Oxidation States

Oxidation State of Sulfur	Compounds
+6	SO ₃ , H ₂ SO ₄ , SO ₄ ²⁻ , SF ₆
+4	SO ₂ , HSO ₃ ⁻ , SO ₃ ²⁻ , SF ₄
+2	SCl ₂
0	S ₈ and all other forms of elemental sulfur
-2	H ₂ S, S ²⁻

The preparation of sulfur trioxide provides an example of the compromise that often must be made between thermodynamics and kinetics.

The acidic properties of sulfuric acid solutions are discussed in Section 14.7.

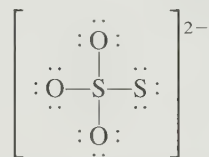
The prefix *thio* means "sulfur."

oxidation state occurs in the metal sulfides and in *hydrogen sulfide* (H₂S), a toxic, foul-smelling gas that acts as a diprotic acid when dissolved in water. Hydrogen sulfide is a strong reducing agent in aqueous solution, producing a milky looking suspension of finely divided sulfur as one of the products. For example, hydrogen sulfide reacts with chlorine in aqueous solution as follows:

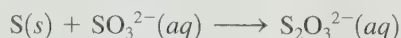


↑
Milky suspension of sulfur

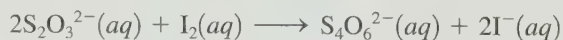
Sulfur also forms the **thiosulfate ion** (S₂O₃²⁻), which has the Lewis structure



Note that this anion can be viewed as a sulfate ion in which one of the oxygen atoms has been replaced by sulfur, which is reflected in the name *thiosulfate*. The thiosulfate ion can be formed by heating sulfur with a sulfite salt in aqueous solution:



One important use of thiosulfate ion is in photography, where S₂O₃²⁻ dissolves solid silver bromide by forming a complex with the Ag⁺ ion (see the Chemical Impact in Section 20.7). Thiosulfate ion is also a good reducing agent and is often used to analyze for iodine:



where S₄O₆²⁻ is called the *tetrathionate ion*.

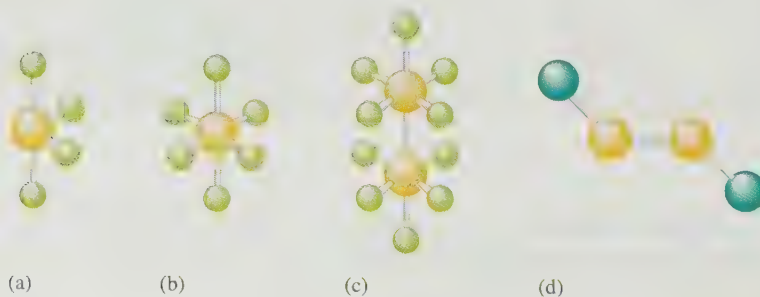


FIGURE 20.22
The structures of (a) SF₄, (b) SF₆,
(c) S₂F₁₀, and (d) S₂Cl₂.

Sulfur reacts with the halogens to form a variety of compounds, such as S_2Cl_2 , SF_4 , SF_6 , and S_2F_{10} . The structures of these molecules are shown in Fig. 20.22.

20.7 The Group 7A Elements

7A
F
Cl
Br
I
At

In our coverage of the representative elements, we have progressed from groups of metallic elements (Groups 1A and 2A), through groups in which the lighter members are nonmetals and the heavier members are metals (Groups 3A, 4A, and 5A), to a group of all nonmetals (Group 6A—although some might prefer to call polonium a metal). The Group 7A elements, the **halogens** (with the valence-electron configuration ns^2np^5), are also all nonmetals whose properties generally vary smoothly going down the group. The only notable exceptions are the unexpectedly low values for the electron affinity of fluorine and the bond energy of the F_2 molecule (see Section 19.1). Table 20.6 summarizes the trends in some physical properties of the halogens.

Because of their high reactivities, the halogens are not found as the free elements in nature. Instead, they are found as halide ions (X^-) in various minerals and in seawater (see Table 20.7).

Although astatine is a member of Group 7A, its chemistry is of no practical importance because all its known isotopes are radioactive. The longest-lived isotope, ^{210}At , has a half-life of only 8.3 hours.

TABLE 20.6 Trends in Selected Physical Properties of the Group 7A Elements

Element	Electro-negativity	Radius of X^- (pm)	$E^\circ(\text{V})$ for $\text{X}_2 + 2\text{e}^- \rightarrow 2\text{X}^-$	Bond Energy of X_2 (kJ/mol)
Fluorine	4.0	136	2.87	154
Chlorine	3.0	181	1.36	239
Bromine	2.8	185	1.09	193
Iodine	2.5	216	0.54	149
Astatine	2.2	—	—	—

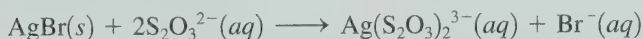
TABLE 20.7 Some Physical Properties, Sources, and Methods of Preparation for the Group 7A Elements

Element	Color and State	Percentage of Earth's Crust	Melting Point ($^\circ\text{C}$)	Boiling Point ($^\circ\text{C}$)	Sources	Method of Preparation
Fluorine	Pale yellow gas	0.07	-220	-188	Fluorospars (CaF_2), cryolite (Na_3AlF_6), fluorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$)	Electrolysis of molten KHF_2
Chlorine	Yellow-green gas	0.14	-101	-34	Rock salt (NaCl), halite (NaCl), sylvite (KCl)	Electrolysis of aqueous NaCl
Bromine	Red-brown liquid	2.5×10^{-4}	-7.3	59	Seawater, brine wells	Oxidation of Br^- by Cl_2
Iodine	Violet-black solid	3×10^{-5}	113	184	Seaweed, brine wells	Oxidation of I^- by electrolysis or MnO_2

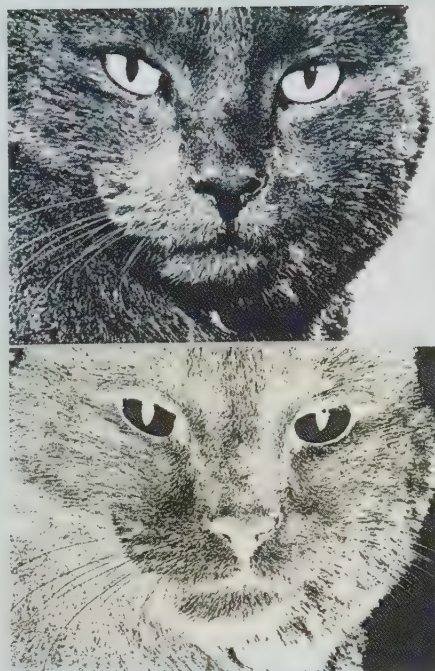
CHEMICAL IMPACT

Photography

In black-and-white photography, light from an object is focused onto a special paper containing an emulsion of solid silver bromide. Silver salts turn dark when exposed to light because the radiant energy stimulates the transfer of an electron to the Ag^+ ion, forming an atom of elemental silver. When photographic paper (film) is exposed to light, the areas exposed to the brightest light form the most silver atoms. The next step is the application of a chemical reducing agent to the film, a process called *developing*. The real advantage of silver-based films is that the silver atoms already present from exposure to light catalyze the reduction of millions of Ag^+ ions in the immediate vicinity in the developing process. Thus the effect of exposure to light is greatly intensified in this chemical reduction process. Once the image has been developed, the unchanged solid silver bromide must be removed so that the film is no longer light-sensitive and the image is fixed. A solution of sodium thiosulfate (called *hypo*) is used in this *fixing process*:



After the excess silver bromide is dissolved and washed away, the fixed image (the *negative*) is ready to produce the positive print. By shining light through the negative onto a fresh sheet of film and repeating the developing and fixing processes, a black-and-white photograph can be produced.



Positive and negative images.

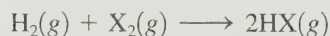


Chlorine, bromine, and iodine.

The halogens, particularly fluorine, have very high electronegativity values (Table 20.6). They tend to form polar covalent bonds with other nonmetals and ionic bonds with metals in their lower oxidation states. When a metal ion is in a higher oxidation state, such as +3 or +4, the metal–halogen bonds are polar covalent ones. For example, TiCl_4 and SnCl_4 are both covalent compounds that are liquids under normal conditions.

Hydrogen Halides

The hydrogen halides can be prepared by a reaction of the elements:



This reaction occurs with explosive vigor when fluorine and hydrogen are mixed. On the other hand, hydrogen and chlorine can coexist with little apparent reaction for relatively long periods in the dark. However, ultraviolet light causes an explosively fast reaction, and this is the basis of a popular lecture demonstration, the “hydrogen–chlorine cannon.” Bromine and iodine also react with hydrogen, but more slowly.

The hydrogen halides also can be prepared by treating halide salts with acid. For example, hydrogen fluoride and hydrogen chloride can be prepared as follows:





A candle burning in an atmosphere of $\text{Cl}_2(g)$. The exothermic reaction, which involves breaking C—C and C—H bonds in the wax and forming C—Cl bonds in their places, produces enough heat to make the gases in the region incandescent (a flame results).

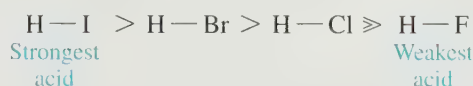
TABLE 20.8 Some Physical Properties of the Hydrogen Halides

HX	Melting Point ($^{\circ}\text{C}$)	Boiling Point ($^{\circ}\text{C}$)	H—X Bond Energy (kJ/mol)
HF	−83	20	565
HCl	−114	−85	427
HBr	−87	−67	363
HI	−51	−35	295

Sulfuric acid is capable of oxidizing Br^- to Br_2 and I^- to I_2 and so cannot be used to prepare hydrogen bromide and hydrogen iodide. However, phosphoric acid, a nonoxidizing acid, can be used to treat bromides and iodides to form the corresponding hydrogen halides.

Some physical properties of the hydrogen halides are listed in Table 20.8. Note the very high boiling point for hydrogen fluoride, which results from extensive hydrogen bonding among the very polar HF molecules (Fig. 20.23). Fluoride ion has such a high affinity for protons that in concentrated aqueous solutions of hydrogen fluoride, the ion $[\text{F}—\text{H}—\text{F}]^-$ exists, in which an H^+ ion is centered between two F^- ions.

When dissolved in water, the hydrogen halides behave as acids, and all except hydrogen fluoride are completely dissociated. Because water is a much stronger base than Cl^- , Br^- , or I^- ion, the acid strengths of HCl, HBr, and HI cannot be differentiated in water. However, in a less basic solvent, such as glacial (pure) acetic acid, the acids show different strengths of the order



To see why hydrogen fluoride is the only weak acid in water among the HX molecules, let's consider the dissociation equilibrium



where

$$K_a = \frac{[\text{H}^+][\text{X}^-]}{[\text{HX}]}$$

from a thermodynamic point of view. Recall that acid strength is reflected by the magnitude of K_a —a small K_a value means a weak acid. Also recall that the value of an equilibrium constant depends on the standard free energy change for the reaction as follows:

$$\Delta G^{\circ} = -RT \ln(K)$$

As ΔG° becomes more negative, K becomes larger; a *decrease* in free energy favors a given reaction. As we saw in Chapter 16, free energy depends on enthalpy, entropy, and temperature. For a process at constant temperature,

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$

Thus, to explain the various acid strengths of the hydrogen halides, we must focus on the factors that determine ΔH° and ΔS° for the acid dissociation reaction.

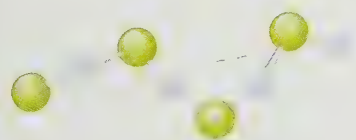


FIGURE 20.23
The hydrogen bonding among HF molecules in liquid hydrogen fluoride.

TABLE 20.9
The Enthalpies and Entropies
of Hydration for the Halide
Ions

X^-	$X^-(g) \xrightarrow{H_2O} X^-(aq)$	
	ΔH° (kJ/mol)	ΔS° (J/K · mol)
F^-	-510	-159
Cl^-	-366	-96
Br^-	-334	-81
I^-	-291	-64

What energy terms are important in determining ΔH° for the dissociation of HX in water? (Keep in mind that large positive contributions to the value of ΔH° will tend to make ΔG° more highly positive, K_a smaller, and the acid weaker.) One important factor is certainly the H—X bond strength. Note from Table 20.8 that the H—F bond is much stronger than the other H—X bonds. This factor tends to make HF a weaker acid than the others.

Another important contribution to ΔH° is the enthalpy of hydration (see Section 11.2) of X^- (see Table 20.9). As we would expect, the smallest of the halide ions, F^- , has the most negative value—its hydration is the most exothermic. This term favors the dissociation of HF into its ions more so than it does for the other HX molecules.

So far we have two conflicting factors: The large HF bond energy tends to make HF a weaker acid than the other hydrogen halides, but the enthalpy of hydration favors the dissociation of HF more than that of the others. In comparing data for HF and HCl, the difference in bond energy (138 kJ/mol) is slightly smaller than the difference in the enthalpies of hydration for the anions (144 kJ/mol). If these were the *only* important factors, HF should be a stronger acid than HCl because the large enthalpy of hydration of F^- more than makes up for the large HF bond strength.

As it turns out, *the deciding factor is entropy*. Note from Table 20.9 that the entropy of hydration for F^- is much more negative than for the other halides because of the high degree of ordering that occurs as the water molecules associate with the small F^- ion. Remember that a negative change in entropy is unfavorable. Thus, although the enthalpy of hydration favors dissociation of HF, the *entropy* of hydration strongly opposes it.

When all these factors are taken into account, ΔG° for the dissociation of HF in water is positive; that is, K_a is small. In contrast, ΔG° for dissociation of the other HX molecules in water is negative (K_a is large). This example illustrates the complexity of the processes that occur in aqueous solutions and the importance of entropy effects in that medium.

In practical terms, **hydrochloric acid** is the most important of the **hydrohalic acids**, the aqueous solutions of the hydrogen halides. About 3 million tons of hydrochloric acid are produced annually for use in cleaning steel before galvanizing and in the manufacture of many other chemicals.

Hydrofluoric acid is used to etch glass by reacting with the silica in glass to form the volatile gas SiF_4 :



When H_2O molecules cluster around an ion, an ordering effect occurs, and ΔS°_{hyd} is negative.

Hydration becomes more exothermic as the charge density of an ion increases. Thus, for ions of a given charge, the smallest is most strongly hydrated.

Stomach acid is 0.1 M HCl.



This Steuben glass design was etched using hydrofluoric acid.

TABLE 20.10 The Known Oxyacids of the Halogens*

Oxidation State of Halogen	Fluorine	Chlorine	Bromine	Iodine*	General Name of Acids	General Name of Salts
+1	HO $\overset{+}{F}$ ***	HOCl	HOBr	HOI	Hypohalous acid	Hypohalites, MOX
+3	**	HOClO	**	**	Halous acid	Halites, MXO ₂
+5	**	HOClO ₂	HOBrO ₂	HOIO ₂	Halic acid	Halates, MXO ₃
+7	**	HOClO ₃	HOBrO ₃	HOIO ₃	Perhalic acid	Perhalates, MXO ₄

* Iodine also forms H₄I₂O₉ (mesodiperic acid) and H₅IO₆ (paraperiodic acid).

** Compound is unknown.

*** HOF oxidation state is best represented as -1 .

Oxyacids and Oxyanions

All the halogens except fluorine combine with various numbers of oxygen atoms to form a series of oxyacids, as shown in Table 20.10. The strengths of these acids vary in direct proportion to the number of oxygen atoms attached to the halogen, as we discussed in Section 14.9.

The only member of the chlorine series that has been obtained in the pure state is *perchloric acid* (HOClO₃), a strong acid and powerful oxidizing agent. Because perchloric acid reacts explosively with many organic materials, it must be handled with great caution. The other oxyacids of chlorine are known only in solution, although salts containing their anions are well known (Fig. 20.24).

Hypochlorous acid (HOCl) is formed when chlorine gas is dissolved in cold water:

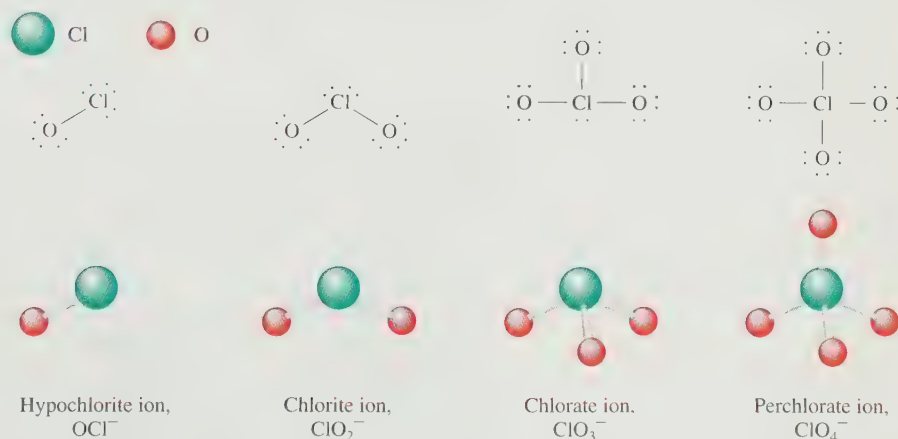
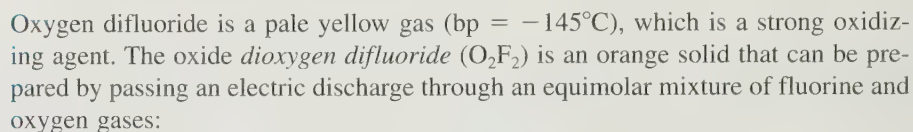


FIGURE 20.24
The structures of the oxychloro anions.

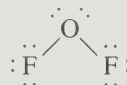
Chlorate salts, such as KClO_3 , are also strong oxidizing agents and are used as weed killers and as oxidizers in fireworks (see Chapter 7) and explosives.

The name for OF_2 is *oxygen difluoride* rather than difluorine oxide because fluorine has a higher electronegativity than oxygen and thus is named as if it were an anion.



Give the Lewis structure, molecular structure, and hybridization of the oxygen atom for OF_2 .

The OF_2 molecule has 20 valence electrons and the Lewis structure is



See Exercise 20.35.

The halogens react readily with most nonmetals to form a variety of compounds, some of which are shown in Table 20.11 on the following page.

$$\text{ICl}(s) + \text{H}_2\text{O}(l) \longrightarrow \text{H}^+(aq) + \text{Cl}^-(aq) + \text{HOI}(aq)$$

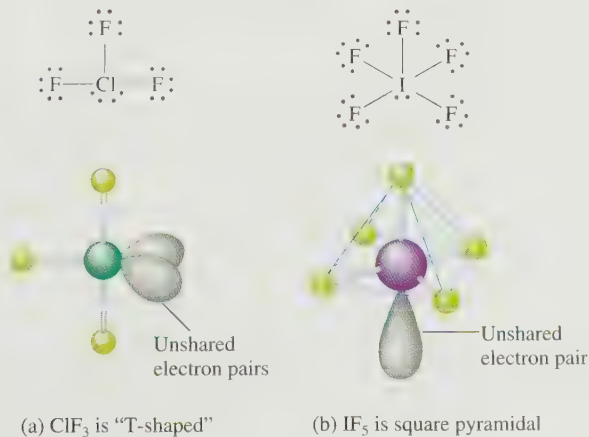
TABLE 20.11 Some Compounds of the Halogens with Nonmetals

Compounds with Group 3A Nonmetals	Compounds with Group 4A Nonmetals	Compounds with Group 5A Nonmetals	Compounds with Group 6A Nonmetals	Compounds with Group 7A Nonmetals
BX_3 ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$)	CX_4 ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$)	NX_3 ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$)	OF_2	ICl
BF_4^-		N_2F_4	O_2F_2	IBr
	SiF_4		OCl_2	BrF
	SiF_6^{2-}	PX_3 ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$)	OBr_2	BrCl
	SiCl_4	PF_5		ClF
		PCl_3	SF_2	
	GeF_4	PBr_3	SCl_2	ClF_3
	GeF_6^{2-}		S_2F_2	BrF_3
	GeCl_4	AsF_3	S_2Cl_2	ICl_3
		AsF_5	SF_4	IF_3
			SCl_4	
		SbF_3	SF_6	ClF_5
		SbF_5		BrF_5
			SeF_4	IF_5
			SeF_6	
			SeCl_2	IF_7
			SeCl_4	
			SeBr_4	
			TeF_4	
			TeF_6	
			TeCl_4	
			TeBr_4	
			TeI_4	

20.8 The Group 8A Elements

The Group 8A elements, the **noble gases**, are characterized by filled s and p valence orbitals (electron configuration of $2s^2$ for helium and ns^2np^6 for the others). Because of this, these elements are very unreactive. In fact, no noble gas compounds were

8A
He
Ne
Ar
Kr
Xe
Rn

**FIGURE 20.25**

The idealized structures of the interhalogens ClF_3 and IF_5 . In reality, the lone pairs cause the bond angles to be slightly less than 90 degrees.

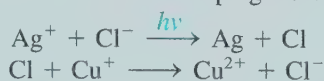
CHEMICAL IMPACT

Automatic Sunglasses

Sunglasses can be troublesome. It seems they are always getting lost or sat on. One solution to this problem for people who wear glasses is photochromic glass—glass that darkens in response to intense light. Recall that glass is a complex, noncrystalline material that is composed of polymeric silicates (see Chapter 10). Of course, glass transmits visible light—its transparency is its most useful property.

Glass can be made photochromic by adding tiny silver chloride crystals that get trapped in the glass matrix as the glass solidifies. Silver chloride has the unusual property of darkening when struck by light—the property that makes the silver halide salts so useful for photographic films. This darkening occurs because light causes an electron transfer from Cl^- to Ag^+ in the silver chloride crystal, forming a silver atom and a chlorine atom. The silver atoms formed in this way tend to migrate to the surface of the silver chloride crystal, where they aggregate to form a tiny crystal of silver metal, which is opaque to light.

In photography the image defined by the grains of silver is fixed by chemical treatment so that it remains permanent. However, in photochromic glass this process must be reversible—the glass must become fully transparent again when the person goes back indoors. The secret to the reversibility of photochromic glass is the presence of Cu^+ ions. The added Cu^+ ions serve two important functions. First, they reduce the Cl atoms formed in the light-induced reaction. This prevents them from escaping from the crystal:



Glasses with photosensitive lenses. The right lens has been exposed to light and the left one has not.

Second, when the exposure to intense light ends (the person goes indoors), the Cu^{2+} ions migrate to the surface of the silver chloride crystal, where they accept electrons from silver atoms as the tiny crystal of silver atoms disintegrates:



The Ag^+ ions are re-formed in this way, then return to their places in the silver chloride crystal, making the glass transparent once again.

Typical photochromic glass decreases to about 20% transmittance (transmits 20% of the light that strikes it) in strong sunlight, and then over a period of a few minutes returns to about 80% transmittance indoors (normal glass has 92% transmittance).

known 50 years ago. Selected properties of the Group 8A elements are summarized in Table 20.12.

Helium was identified by its characteristic emission spectrum as a component of the sun before it was found on earth. The major sources of helium on earth are natural gas deposits, where helium was formed from α -particle decay of radioactive elements. The α particle is a helium nucleus that can easily pick up electrons from the environment to form a helium atom. Although helium forms no compounds, it is an important substance that is used as a coolant, as a pressurizing gas for rocket fuels, as a diluent in the gases used for deep-sea diving and spaceship atmospheres, and as the gas in lighter-than-air airships (blimps).

Like helium, *neon* and *argon* form no compounds but are used extensively. For example, neon is employed in luminescent lighting (neon signs), and argon is used to provide the noncorrosive atmosphere in incandescent light bulbs, which prolongs the life of the tungsten filament.



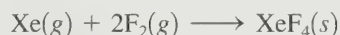
Neon, a noble gas, is used in luminescent lighting (neon signs).

TABLE 20.12 Selected Properties of Group 8A Elements

Element	Melting Point (°C)	Boiling Point (°C)	Atmospheric Abundance (% by Volume)	Examples of Compounds
Helium	-270	-269	5×10^{-4}	None
Neon	-249	-246	1×10^{-3}	None
Argon	-189	-186	9×10^{-1}	None
Krypton	-157	-153	1×10^{-4}	KrF ₂
Xenon	-112	-107	9×10^{-6}	XeF ₄ , XeO ₃ , XeF ₆

Of the Group 8A elements, only *krypton* and *xenon* have been observed to form chemical compounds. The first of these was prepared in 1962 by Neil Bartlett, an English chemist who used Xe(g) and PtF₆(g) to make the ionic compound with the empirical formula XePtF₆.

Less than a year after Bartlett's report of XePtF₆, a group at Argonne National Laboratory near Chicago prepared xenon tetrafluoride by reaction of xenon and fluorine gases in a nickel reaction vessel at 400°C and 6 atm:



Xenon tetrafluoride forms stable colorless crystals. Two other xenon fluorides, XeF₂ and XeF₆, were synthesized by the group at Argonne, and a highly explosive xenon oxide (XeO₃) also was found. The xenon fluorides react with water to form hydrogen fluoride and oxycompounds; for example,



In the past 40 years, other xenon compounds have been prepared, for example, XeO₄ (explosive), XeO₂F₄, XeO₂F₂, and XeO₃F₂. These compounds contain discrete molecules with covalent bonds between the xenon and the other atoms. The structures of some of these xenon compounds are summarized in Fig. 20.26. A few compounds of krypton, such as KrF₂ and KrF₄, also have been observed. There is evidence that radon also reacts with fluorine, but the radioactivity of radon makes its chemistry very difficult to study.

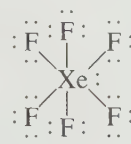
SAMPLE EXERCISE 20.6

The Structure of XeF₆

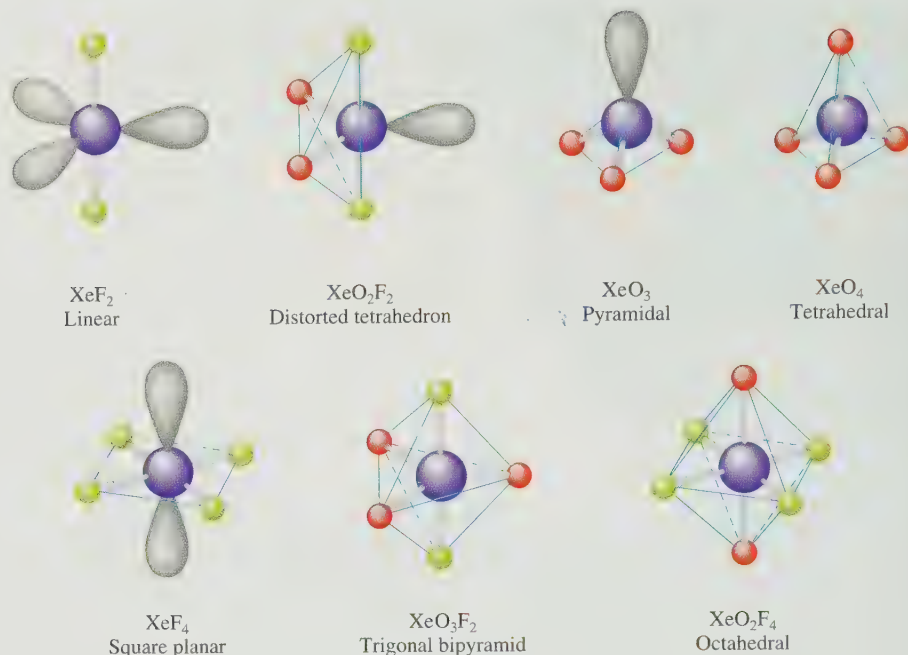
Use the VSEPR model to predict whether XeF₆ has an octahedral structure.

SOLUTION

The XeF₆ molecule contains 50 [8 + 6(7)] valence electrons and the Lewis structure is



The xenon atom has seven pairs of electrons around it (one lone pair and six bonding pairs), one more pair than can be accommodated in an octahedral arrangement.

**FIGURE 20.26**

The structures of several known xenon compounds.

Thus XeF_6 will not have an octahedral structure, but should be distorted from this geometry by the extra electron pair. There is experimental evidence that the structure of XeF_6 is not octahedral.

See Exercises 20.41 and 20.42.

For Review

Summary

The Group 5A elements show remarkably varied chemical properties. Nitrogen and phosphorus are nonmetals and can form 3− anions in salts with active metals. Antimony and bismuth tend to be metallic, although no ionic compounds with their 5+ ions are known. The compounds containing bismuth(V) or antimony(V) are molecular rather than ionic. All the Group 5A members except nitrogen form molecules with five covalent bonds. The ability of these elements to form π bonds decreases dramatically after nitrogen. Thus phosphorus, arsenic, and antimony exist in the gas phase as aggregates of more than two atoms.

The strength of the triple bond in the N_2 molecule is of great importance both thermodynamically and kinetically. Most binary nitrogen-containing compounds decompose exothermically to the elements, a fact that explains the power of nitrogen-based explosives.

The nitrogen cycle is composed of a series of steps describing how nitrogen is cycled in the natural environment. One step involves the transformation of nitrogen gas in the atmosphere into nitrogen-containing compounds useful to plants, a process called nitrogen fixation. The Haber process is one example of nitrogen fixation; another is provided by nitrogen-fixing bacteria in the root nodules of certain plants. Denitrification is the reverse process—the release of nitrogen gas back into the atmosphere.

Key Terms

Section 20.2

Haber process
 nitrogen fixation
 nitrogen-fixing bacteria
 denitrification
 nitrogen cycle
 ammonia
 hydrazine
 nitric acid
 Ostwald process

Section 20.3

phosphoric (orthophosphoric) acid
 condensation reactions
 phosphorous acid
 superphosphate of lime

Section 20.5

ozone
ozonolysis

Section 20.6

Frasch process
sulfuric acid
thiosulfate ion

Section 20.7

halogens
hydrochloric acid
hydrohalic acids
disproportionation reaction
interhalogen compounds

Section 20.8

noble gases

Ammonia, the most important nitrogen hydride, has pyramidal molecules with polar bonds. Hydrazine (N_2H_4) is a powerful reducing agent. Nitrogen forms a series of oxides in which it has an oxidation state ranging from 1 to 5; the most important are nitric oxide and nitrogen dioxide. Nitric acid (HNO_3) is an important strong acid made by the Ostwald process, in which ammonia is first oxidized to nitric oxide, which is then oxidized to nitrogen dioxide, which is dissolved in water to form nitric acid. Nitrous acid (HNO_2) is a weak acid.

Phosphorus exists in three elemental forms: white, black, and red. Although it has a lower electronegativity than nitrogen, phosphorus forms the P^{3-} anion in phosphides. Phosphine (PH_3) has a structure analogous to that of ammonia but with bond angles close to 90° . Phosphorus reacts with oxygen to form P_4O_6 (oxidation state of +3) and P_4O_{10} (oxidation state of +5). When P_4O_{10} dissolves in water, it forms phosphoric acid (H_3PO_4), a weak acid. Phosphoric acid readily undergoes condensation reactions, giving up water molecules to form polymeric acids.

The Group 6A elements show the usual tendency of increasing metallic properties going down the group. However, none behaves as a typical metal. Most commonly, these elements achieve noble gas configurations by adding two electrons to form $2-$ anions. Group 6A elements also can form covalent bonds with other nonmetals.

Oxygen exists in two elemental forms, O_2 and ozone (O_3), a V-shaped molecule. Ozone is a powerful oxidizing agent with important environmental implications.

Sulfur also exists in two elemental forms, rhombic and monoclinic, both of which contain stacks of S_8 rings. Sulfur occurs in nature both as the free element and in ores as sulfides and sulfates. Sulfur forms three oxides. Sulfur monoxide (SO) is unstable. When sulfur dioxide (SO_2) is dissolved in water, sulfurous acid (H_2SO_3) forms, which is analogous in many respects to carbonic acid as a weak acid. Sulfur trioxide (SO_3) dissolves in water to form sulfuric acid (H_2SO_4), an extremely important industrial chemical and a strong acid that is a powerful dehydrating agent. Sulfur forms a variety of compounds in which it has a +6, +4, +2, 0, or -2 oxidation state.

The Group 7A elements, the halogens, are all nonmetals. The halogens form hydrogen halides (HX) that behave as strong acids in water, except for hydrogen fluoride. Hydrofluoric acid is a weak acid because of the strong $\text{H}-\text{F}$ bond and because the entropy of hydration for the F^- ion is much more negative than it is for the other halide ions. The oxyacids of the halogens become stronger as the number of oxygen atoms attached to the halogen increases. Interhalogens are compounds of two different halogens.

The noble gases of Group 8A are characterized by filled valence shells and are generally unreactive. Krypton, xenon, and radon do, however, form compounds with the highly electronegative atoms fluorine and oxygen.

A blue question or exercise number indicates that the answer to that question or exercise appears at the back of this book and a solution appears in the *Solutions Guide*.

Questions

1. The synthesis of ammonia gas from nitrogen gas and hydrogen gas represents a classic case in which a knowledge of kinetics and equilibrium was used to make a desired chemical

reaction economically feasible. Explain how each of the following conditions helps to maximize the yield of ammonia.

- a. running the reaction at an elevated temperature
 - b. removing the ammonia from the reaction mixture as it forms
 - c. using a catalyst
 - d. running the reaction at high pressure
2. White phosphorus is much more reactive than black or red phosphorus. Explain.

3. In many natural waters, nitrogen and phosphorus are the least abundant nutrients available for plant life. Some waters that become polluted from agricultural runoff or municipal sewage become infested with algae. The algae consume most of the dissolved oxygen in the water, and fish life dies off as a result. Describe how these events are chemically related.
4. Ozone is desirable in the upper atmosphere and undesirable in the lower atmosphere. A dictionary states that ozone has the scent of a fresh spring day. How can these seemingly conflicting statements be reconciled in terms of the chemical properties of ozone?
5. Describe the structural changes that occur when plastic sulfur becomes brittle.
6. Sulfur dissolves in an aqueous solution that contains sulfide ion. Sulfur will then precipitate from this solution if nitric acid is added. Explain.
7. Give two reasons why F_2 is the most reactive of the halogens.
8. Explain why HF is a weak acid, whereas HCl, HBr, and HI are all strong acids.
9. Although He is the second most abundant element in the universe, it is very rare on earth. Why?
10. The noble gases were among the latest elements discovered; their existence was not predicted by Mendeleev when he published his first periodic table. Explain. In chemistry textbooks written before 1962 the noble gases were referred to as the inert gases. Why do we no longer use this term?

Exercises

In this section similar exercises are paired.

Group 5A Elements

11. The oxyanion of nitrogen in which it has the highest oxidation state is the nitrate ion (NO_3^-). The corresponding oxyanion of phosphorus is PO_4^{3-} . The NO_4^{3-} ion is known but not very stable. The PO_3^{3-} ion is not known. Account for these differences in terms of the bonding in the four anions.
12. In each of the following pairs of substances, one is stable and known, and the other is unstable. For each pair, choose the stable substance, and explain why the other is unstable.
 - a. NF_5 or PF_5
 - b. AsF_5 or AsI_5
 - c. NF_3 or NBr_3
13. Complete and balance each of the following reactions.
 - a. the decomposition of solid ammonium nitrate
 - b. the decomposition of gaseous dinitrogen pentoxide
 - c. the reaction between solid potassium phosphide and water
 - d. the reaction between liquid phosphorus tribromide and water
 - e. the reaction between aqueous ammonia and aqueous sodium hypochlorite
14. Arsenic reacts with oxygen to form oxides that react with water in a manner analogous to that of the phosphorus oxides. Write balanced chemical equations describing the reaction of

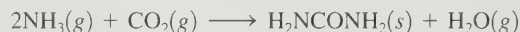
arsenic with oxygen and the reaction of the resulting oxide with water.

15. Phosphorus occurs naturally in the form of fluorapatite, $CaF_2 \cdot Ca_3(PO_4)_2$, where the dot indicates 1 part CaF_2 to 3 parts $Ca_3(PO_4)_2$. This mineral is reacted with an aqueous solution of sulfuric acid in the preparation of a fertilizer. The products are phosphoric acid, hydrogen fluoride, and gypsum, $CaSO_4 \cdot 2H_2O$. Write and balance the chemical equation describing this process.
16. Lewis structures can be used to understand why some molecules react in certain ways. Write the Lewis structure for the reactants and products in the reactions described below.
 - a. Nitrogen dioxide dimerizes to produce dinitrogen tetroxide.
 - b. Boron trifluoride accepts a pair of electrons from ammonia, forming BF_3NH_3 .
 Give a possible explanation for why these two reactions occur.
17. Air bags are activated when a severe impact causes a steel ball to compress a spring and electrically ignite a detonator cap. This causes sodium azide (NaN_3) to decompose explosively according to the following reaction:



How many moles of $NaN_3(s)$ must be reacted to inflate an air bag to 70.0 L at STP?

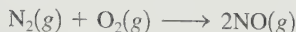
18. Urea (H_2NCONH_2) is used extensively as a nitrogen source in fertilizers. It is produced commercially from the reaction of ammonia and carbon dioxide:



Ammonia gas at 223°C and 90. atm flows into a reactor at a rate of 500. L/min. Carbon dioxide at 223°C and 45 atm flows into the reactor at a rate of 600. L/min. What mass of urea is produced per minute by this reaction assuming a 100% yield?

19. Hydrazine (N_2H_4) is used as a fuel in liquid-fueled rockets. When hydrazine reacts with oxygen gas, nitrogen gas and water vapor are produced. Write a balanced equation and use bond energies from Table 8.4 to estimate ΔH for this reaction.
20. The space shuttle orbiter utilizes the oxidation of methylhydrazine by dinitrogen tetroxide for propulsion:

$$4N_2H_3CH_3(l) + 5N_2O_4(l) \longrightarrow 12H_2O(g) + 9N_2(g) + 4CO_2(g)$$
 Calculate ΔH° for this reaction using data in Appendix 4. Compare your answer to the ΔH value determined in Sample Exercise 20.2. Explain any discrepancies.
21. Many oxides of nitrogen have positive values for the standard free energy of formation. Using NO as an example, explain why this is the case.
22. Using data from Appendix 4 calculate ΔH° , ΔS° , and ΔG° for the reaction



Why does NO form in an automobile engine but then does not readily decompose back to N_2 and O_2 in the atmosphere?

23. Compare the Lewis structures with the molecular orbital view of the bonding in NO, NO^+ , and NO^- . Account for any discrepancies between the two models.
24. The energy to break a particular bond is not always constant. It takes about 200 kJ/mol less energy to break the N—Cl bond in NOCl as compared with NCl_3 :



Why is there such a great discrepancy in the apparent N—Cl bond energies? *Hint:* Consider what happens to the nitrogen–oxygen bond in the first reaction.

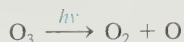
25. Predict the relative acid strengths of the following compounds.
a. H_3PO_4 and H_3PO_3 b. H_3PO_4 , H_2PO_4^- , and HPO_4^{2-}
26. Trisodium phosphate (TSP) is an effective grease remover. Like many cleaners, TSP acts as a base in water. Write a balanced equation to account for this behavior.
27. Isophosphoric acid ($\text{H}_4\text{P}_2\text{O}_6$) and diphosphonic acid ($\text{H}_4\text{P}_2\text{O}_5$) are tri- and diprotic acids, respectively. Draw Lewis structures for these acids that are consistent with these facts.
28. One of the most strongly acidic solutions known is a mixture of antimony pentafluoride (SbF_5) and fluorosulfonic acid (HSO_3F). The dominant equilibria are



- a. Draw Lewis structures for all the species shown in the preceding reactions. Predict the hybridization of the central Sb and S atoms in each structure.
- b. This *superacid* solution is capable of protonating (adding H^+ to) virtually every known organic compound. What is the active protonating agent in the superacid solution?

Group 6A Elements

29. Use bond energies to estimate the maximum wavelength of light that will cause the reaction



30. The xerographic (dry writing) process was invented in 1938 by C. Carlson. In xerography, an image is produced on a photoconductor by exposing it to light. Selenium is commonly used, since its conductivity increases three orders of magnitude upon exposure to light in the range from 400 to 500 nm. What color light should be used to cause selenium to become conductive? (See Figure 7.2.)

31. Complete and balance each of the following reactions.

- a. the reaction between sulfur dioxide gas and oxygen gas

- b. the reaction between sulfur trioxide gas and water
c. the reaction between aqueous sodium thiosulfate and aqueous iodine
d. the reaction between copper metal and aqueous hot sulfuric acid

32. Write a balanced equation describing the reduction of H_2SeO_4 by SO_2 to produce selenium.

33. For each of the following, write the Lewis structure(s), predict the molecular structure (including bond angles), and give the expected hybridization of the central atom.

- a. SO_3^{2-} c. SCl_2 e. TeF_6
b. O_3 d. SeBr_4

34. Disulfur dinitride (S_2N_2) exists as a ring of alternating sulfur and nitrogen atoms. S_2N_2 will polymerize to polythiazyl, which acts as a metallic conductor of electricity along the polymer chain. Write a Lewis structure for S_2N_2 .

Group 7A Elements

35. Write the Lewis structure for O_2F_2 . Predict the bond angles and hybridization of the two central oxygen atoms. Assign oxidation states and formal charges to the atoms in O_2F_2 . The compound O_2F_2 is a vigorous and potent oxidizing and fluorinating agent. Are oxidation states or formal charges more useful in accounting for these properties of O_2F_2 ?

36. For each of the following, write the Lewis structure(s), predict the molecular structure (including bond angles), and give the expected hybridization of the central atom.

- a. Freon-12 (CCl_2F_2) c. iodine trichloride
b. perchloric acid d. bromine pentafluoride

37. Complete and balance each of the following reactions.

- a. $\text{BaCl}_2(\text{s}) + \text{H}_2\text{SO}_4(\text{aq}) \longrightarrow$
b. $\text{BrF}(\text{s}) + \text{H}_2\text{O}(\text{l}) \longrightarrow$
c. $\text{SiO}_2(\text{s}) + \text{HF}(\text{aq}) \longrightarrow$

38. Hypofluorous acid is the most recently prepared of the halogen oxyacids. Weighable amounts were first obtained in 1971 by M. H. Studies and E. N. Appelman using the fluorination of ice. Hypofluorous acid is exceedingly unstable, decomposing spontaneously (with a half-life of 30 min) to HF and O_2 in a Teflon container at room temperature. It reacts rapidly with water to produce HF, H_2O_2 , and O_2 . In dilute acid, H_2O_2 is the major product; in dilute base, O_2 is the major product.

- a. Write balanced equations for the reactions described above.
b. Assign oxidation states to the elements in hypofluorous acid. Does this suggest why hypofluorous acid is so unstable?

39. Hydrazine is somewhat toxic. Use the half-reactions shown below to explain why household bleach (highly alkaline solution of sodium hypochlorite) should not be mixed with household ammonia or glass cleansers that contain ammonia.



40. What is a disproportionation reaction? Use the following reduction potentials



to predict whether HClO_2 will disproportionate.

Group 8A Elements

41. The xenon halides and oxides are isoelectronic with many other compounds and ions containing halogens. Give a molecule or ion in which iodine is the central atom that is isoelectronic with each of the following.

- xenon tetroxide
- xenon trioxide
- xenon difluoride
- xenon tetrafluoride
- xenon hexafluoride

42. For each of the following, write the Lewis structure(s), predict the molecular structure (including bond angles), and give the expected hybridization of the central atom.

- KrF_2
- KrF_4
- XeO_2F_2
- XeO_2F_4

43. Xenon difluoride has proven to be a versatile fluorinating agent. For example, in the reaction



the by-products Xe and HF are easily removed, leaving pure $\text{C}_6\text{H}_5\text{F}$. Xenon difluoride is stored in an inert atmosphere free from oxygen and water. Why is this necessary?

44. Using the data in Table 20.12, calculate the mass of argon at 25°C and 1.0 atm in a room $10.0 \text{ m} \times 10.0 \text{ m} \times 10.0 \text{ m}$. How many Ar atoms are in this room? How many Ar atoms do you inhale in one breath (approximately 2 L) of air at 25°C and 1.0 atm? Argon gas is inert, so it poses no serious health risks. However, if significant amounts of radon were inhaled into the lungs, lung cancer is a possible result. Explain the health-risk differences between argon gas and radon gas.

Additional Exercises

45. The compound NF_3 is quite stable, but NCl_3 is very unstable (NCl_3 was first synthesized in 1811 by P. L. Dulong, who lost three fingers and an eye studying its properties). The compounds NBr_3 and NI_3 are unknown, although the explosive compound $\text{NI}_3 \cdot \text{NH}_3$ is known. Account for the instability of these halides of nitrogen.

46. The N_2O molecule is linear and polar.

- On the basis of this experimental evidence, which arrangement, NNO or NON , is correct? Explain your answer.
- On the basis of your answer in part a, write the Lewis structure of N_2O (including resonance forms). Give the formal charge on each atom and the hybridization of the central atom.
- How would the multiple bonding in $:\text{N} \equiv \text{N} - \ddot{\text{O}}:$ be described in terms of orbitals?

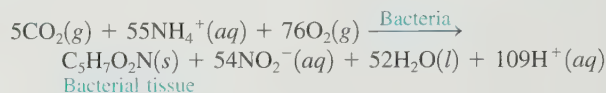
47. Oxidation of the cyanide ion produces the stable cyanate ion, OCN^- . The fulminate ion, CNO^- , on the other hand, is very unstable. Fulminate salts explode when struck; $\text{Hg}(\text{CNO})_2$ is used in blasting caps. Write the Lewis structures and assign formal charges for the cyanate and fulminate ions. Why is the fulminate ion so unstable?

48. Sodium bismuthate (NaBiO_3) is used to test for the presence of Mn^{2+} in solution by the following reaction:



- Balance this equation.
- Given that bismuth does not form double bonds with oxygen in BiO_3^- and that NaBiO_3 is relatively insoluble in water, what type of structure must NaBiO_3 have to account for this behavior?

49. Bacterial digestion is an economical method of sewage treatment. The reaction

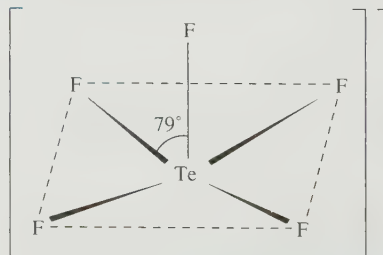


is an intermediate step in the conversion of the nitrogen in organic compounds into nitrate ions. How much bacterial tissue is produced in a treatment plant for every $1.0 \times 10^4 \text{ kg}$ of wastewater containing 3.0% NH_4^+ ions by mass? Assume that 95% of the ammonium ions are consumed by the bacteria.

50. An unknown element is a nonmetal and has a valence electron configuration of ns^2np^4 .

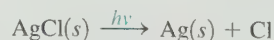
- How many valence electrons does this element have?
- What are some possible identities for this element?
- What is the formula of the compound this element would form with lithium?
- Would this element have a larger or smaller radius than barium?
- Would this element have a greater or smaller ionization energy than fluorine?

51. The structure of TeF_5^- is



Draw a complete Lewis structure for TeF_5^- , and explain the distortion from the ideal square pyramidal structure.

52. Photogray lenses contain small embedded crystals of solid silver chloride. Silver chloride is light-sensitive because of the reaction



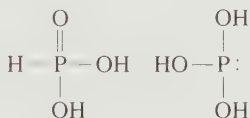
Small particles of metallic silver cause the lenses to darken. In the lenses this process is reversible. When the light is removed, the reverse reaction occurs. However, when pure white silver chloride is exposed to sunlight it darkens; the reverse reaction does not occur in the dark.

- How do you explain this difference?
- Photogray lenses do become permanently dark in time. How do you account for this?

53. Which do you think would be the greater health hazard, the release of a radioactive nuclide of Sr or a radioactive nuclide of Xe into the environment? Assume the amount of radioactivity is the same in each case. Explain your answer on the basis of the chemical properties of Sr and Xe. Why are the chemical properties of a radioactive substance important in assessing its potential health hazards?

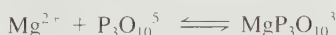
Challenge Problems

54. Many structures of phosphorus-containing compounds are drawn with some P=O bonds. These bonds are not the typical π bonds we've considered, which involve the overlap of two p orbitals. Instead, they result from the overlap of a d orbital on the phosphorus atom with a p orbital on oxygen. This type of π bonding is sometimes used as an explanation for why H_3PO_3 has the first structure below rather than the second:



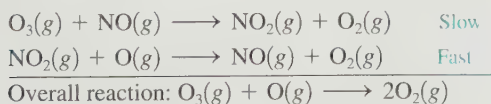
Draw a picture showing how a d orbital and a p orbital overlap to form a π bond.

55. Use bond energies (Table 8.4) to show that the preferred products for the decomposition of N_2O_3 are NO_2 and NO rather than O_2 and N_2O . (The N—O single bond energy is 201 kJ/mol.) *Hint:* Consider the reaction kinetics.
56. Sodium tripolyphosphate ($\text{Na}_5\text{P}_3\text{O}_{10}$) is used in many synthetic detergents to soften the water by complexing Mg^{2+} and Ca^{2+} ions. It also increases the efficiency of surfactants (wetting agents) that lower a liquid's surface tension. The K value for the formation of $\text{MgP}_3\text{O}_{10}^{3-}$ is 4.0×10^8 . The reaction is

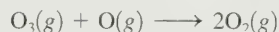


Calculate the concentration of Mg^{2+} in a solution that was originally 50. ppm of Mg^{2+} (50. mg/L of solution) after 40. g $\text{Na}_5\text{P}_3\text{O}_{10}$ is added to 1.0 L of the solution.

57. One pathway for the destruction of ozone in the upper atmosphere is

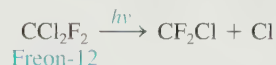


- Which species is a catalyst?
- Which species is an intermediate?
- The activation energy E_a for the uncatalyzed reaction



is 14.0 kJ. E_a for the same reaction when catalyzed by the presence of NO is 11.9 kJ. What is the ratio of the rate constant for the catalyzed reaction to that for the uncatalyzed reaction at 25°C? Assume that the frequency factor A is the same for each reaction.

- One of the concerns about the use of Freons is that they will migrate to the upper atmosphere, where chlorine atoms can be generated by the reaction



Chlorine atoms also can act as a catalyst for the destruction of ozone. The first step of a proposed mechanism for chlorine-catalyzed ozone destruction is



Assuming a two-step mechanism, propose the second step in the mechanism and give the overall balanced equation.

- The activation energy for Cl-catalyzed destruction of ozone is 2.1 kJ/mol. Estimate the efficiency with which Cl atoms destroy ozone as compared with NO molecules at 25°C. Assume that the frequency factor A is the same for each catalyzed reaction and assume similar rate laws for each catalyzed reaction.
58. Using data from Appendix 4, calculate ΔH° , ΔG° , and K_p (at 298 K) for the production of ozone from oxygen:



At 30 km above the surface of the earth, the temperature is about 230. K, and the partial pressure of oxygen is about 1.0×10^{-3} atm. Estimate the partial pressure of ozone in equilibrium with oxygen at 30 km above the earth's surface. Is it reasonable to assume that the equilibrium between oxygen and ozone is maintained under these conditions? Explain.

Marathon Problem

This problem is designed to incorporate several concepts and techniques into one situation. Marathon Problems can be used in class by groups of students to help facilitate problem-solving skills.

59. Captain Kirk has set a trap for the Klingons who are threatening an innocent planet. He has sent small groups of fighter rockets to sites that are invisible to Klingon radar and put a decoy in the open. He calls this the "fishhook" strategy. Mr. Spock has sent a coded message to the chemists on the fighters to tell the ships what to do next. The outline of the message is

(1)	(2)	(3)	(4)	(5)	(6)
(7)	(8)	(9)	(10)	(11)	(12)

Fill in the blanks of the message using the following clues.

- (1) Symbol of the halogen whose hydride has the second highest boiling point in the series of HX compounds that are hydrogen halides.
- (2) Symbol of the halogen that is the only hydrogen halide, HX, that is a weak acid in aqueous solution.
- (3) Symbol of the element whose existence on the sun was known before its existence on earth was discovered.
- (4) Symbol of the element whose presence can interfere with the qualitative analysis for Pb^{2+} , Hg_2^{2+} , and Ag^+ . When chloride ions are added to an aqueous solution of this metal ion, a white precipitate forms with formula $\text{MOC}_2\text{H}_3\text{O}_2$.
- (5) Symbol of the Group 6A element that, like selenium, is a semiconductor.
- (6) Symbol for the element known in rhombic and monoclinic forms.
- (7) Symbol for the element that exists as diatomic molecules in a yellow-green gas when not combined with another element; its silver, lead, and mercury(I) salts are white and insoluble in water.
- (8) Symbol for the most abundant element in and near the earth's crust.
- (9) Symbol for the element that seems to give some protection against cancer when a diet rich in this element is consumed.
- (10) Symbol for the only noble gas besides xenon that has been shown to form compounds under some circumstances (write the symbol backward and split the letters as shown).
- (11) Symbol for the toxic element that, like phosphorus and antimony, forms tetrameric molecules when uncombined with other elements (split the letters of the symbol as shown).

- (12) Symbol for the element that occurs as an inert component of air but is a very prominent part of fertilizers and explosives.



Media Activities

1. Chapter 20 presents the Group 5A, 6A, 7A, and 8A elements. As in Chapter 19, the material to emphasize for each group of elements includes the properties discussed, bonding characteristics, and typical reactions. Read the CD Overview to review important topics covered in Chapter 20.
2. Chapter 20 emphasizes predicting shapes of the various covalent compounds formed by Group 5A–8A elements. To review predicting shapes of molecules, work through the VSEPR Theory of Molecular Structure Understanding Concepts activity on the student CD. The text uses the term *distorted tetrahedron* to describe the shape of XeO_2F_2 . What term is used in the activity to describe XeO_2F_2 ?
3. The most important hydride of nitrogen is ammonia. What is the major use of NH_3 ? What are the acid–base properties of NH_3 ? Would you expect NH_3 to be soluble in water? Why? Open the Ammonia Fountain Visualization on the student CD. Explain why water fills the ammonia container in this demonstration. (*Hint:* Think about what happens to the pressure of NH_3 in the ammonia container as water is squirted into this container.)
4. Test your understanding of Chapter 20 material by taking the ACE quizzes on the student web site.



For additional web activities and other resources, visit the Zumdahl, *Chemistry*, Sixth Edition textbook site at <http://chemistry.college.hmco.com/students>.



Transition Metals and Coordination Chemistry

Transition metals have many uses in our society. Iron is used for steel; copper for electrical wiring and water pipes; titanium for paint; silver for photographic paper; manganese, chromium, vanadium, and cobalt as additives to steel; platinum for industrial and automotive catalysts; and so on.

One indication of the importance of transition metals is the great concern shown by the U.S. government for continuing the supply of these elements. In recent years the United States has been a net importer of about 60 “strategic and critical” minerals, including cobalt, manganese, platinum, palladium, and chromium. All these metals play a vital role in the U.S. economy and defense, and approximately 90% of the required amounts must be imported (see Table 21.1).

In addition to being important in industry, transition metal ions play a vital role in living organisms. For example, complexes of iron provide for the transport and storage of oxygen, molybdenum and iron compounds are catalysts in nitrogen fixation, zinc is found in more than 150 biomolecules in humans, copper and iron play a crucial role in the respiratory cycle, and cobalt is found in essential biomolecules such as vitamin B₁₂.

In this chapter we explore the general properties of transition metals, paying particular attention to the bonding, structure, and properties of the complex ions of these metals.

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- 21.2 The First-Row Transition Metals**
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 - Structural Isomerism
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 - Hydrometallurgy
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 - Heat Treatment of Steel

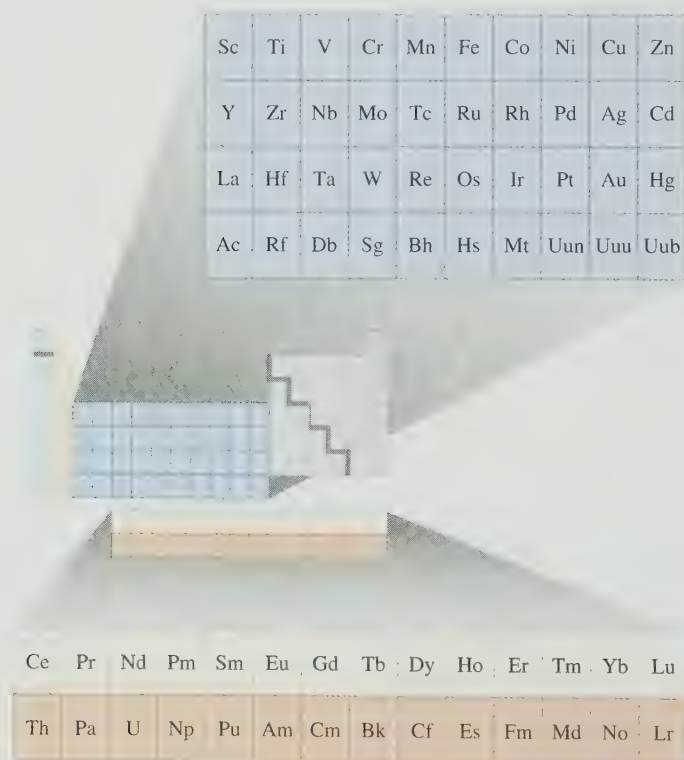
TABLE 21.1 Some Transition Metals Important to the U.S. Economy and Defense

Metal	Uses	Percentage Imported
Chromium	Stainless steel (especially for parts exposed to corrosive gases and high temperatures)	~91%
Cobalt	High-temperature alloys in jet engines, magnets, catalysts, drill bits	~93%
Manganese	Steelmaking	~97%
Platinum and palladium	Catalysts	~87%

21.1 The Transition Metals: A Survey

General Properties

One striking characteristic of the representative elements is that their chemistry changes markedly across a given period as the number of valence electrons changes. The chemical similarities occur mainly within the vertical groups. In contrast, *the transition metals show great similarities within a given period as well as within a given vertical group*. This difference occurs because the last electrons added for transition metals are inner electrons: *d* electrons for the *d*-block transition metals



Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
Ac	Rf	Db	Sg	Bh	Hs	Mt	Uun	Uuu	Uub

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr



Sterling silver candlesticks and bowl from Japan.

and *f* electrons for the lanthanides and actinides. These inner *d* and *f* electrons cannot participate as easily in bonding as can the valence *s* and *p* electrons. Thus the chemistry of the transition elements is not affected as greatly by the gradual change in the number of electrons as is the chemistry of the representative elements.

Group designations are traditionally given on the periodic table for the *d*-block transition metals (see Fig. 21.1). However, these designations do not relate as directly to the chemical behavior of these elements as they do for the representative elements (the A groups), so we will not use them.

As a class, the transition metals behave as typical metals, possessing metallic luster and relatively high electrical and thermal conductivities. Silver is the best conductor of heat and electric current. However, copper is a close second, which explains copper's wide use in the electrical systems of homes and factories.

Despite their many similarities, the transition metals do vary considerably in certain properties. For example, tungsten has a melting point of 3400°C and is used for filaments in light bulbs; mercury is a liquid at 25°C . Some transition metals such as iron and titanium are hard and strong and make very useful structural materials; others such as copper, gold, and silver are relatively soft. The chemical reactivity of the transition metals also varies significantly. Some react readily with oxygen to form oxides. Of these metals, some, such as chromium, nickel, and cobalt, form oxides that adhere tightly to the metallic surface, protecting the metal from further oxidation. Others, such as iron, form oxides that scale off, constantly exposing new metal to the corrosion process. On the other hand, the noble metals—primarily gold, silver, platinum, and palladium—do not readily form oxides.

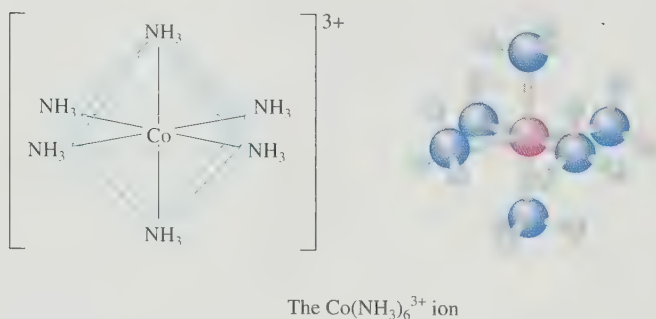
In forming ionic compounds with nonmetals, the transition metals exhibit several typical characteristics:

More than one oxidation state is often found. For example, iron combines with chlorine to form FeCl_2 and FeCl_3 .

	<i>f</i> -block transition elements													
*Lanthanides	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
†Actinides	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

FIGURE 21.1
The position of the transition elements on the periodic table. The *d*-block elements correspond to filling the 3*d*, 4*d*, 5*d*, or 6*d* orbitals. The inner transition metals correspond to filling the 4*f* (lanthanides) or 5*f* (actinides) orbitals.

The cations are often **complex ions**, species where *the transition metal ion is surrounded by a certain number of ligands* (molecules or ions that behave as Lewis bases). For example, the compound $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ contains the $\text{Co}(\text{NH}_3)_6^{3+}$ cation and Cl^- anions.



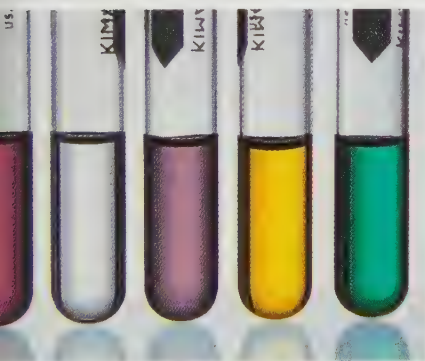
Most compounds are colored, because the transition metal ion in the complex ion can absorb visible light of specific wavelengths.

Many compounds are paramagnetic (they contain unpaired electrons).

In this chapter we will concentrate on the **first-row transition metals** (scandium through zinc) because they are representative of the other transition series and because they have great practical significance. Some important properties of these elements are summarized in Table 21.2 and are discussed in the next section.



(clockwise from upper left) Calcite stalactites colored by traces of iron. Quartz is often colored by the presence of transition metals such as Mn, Fe, and Ni. Wulfenite contains PbMoO_4 . Rhodochrosite is a mineral containing MnCO_3 .



(from left to right) Aqueous solutions containing the metal ions Co^{2+} , Mn^{2+} , Cr^{3+} , Fe^{3+} , and Ni^{2+} .

Chromium has the electron configuration $[\text{Ar}]4s^13d^5$.

A set of orbitals with the same energy is said to be *degenerate*.

Electron Configurations

The electron configurations of the first-row transition metals were discussed in Section 7.11. The $3d$ orbitals begin to fill after the $4s$ orbital is complete, that is, after calcium ($[\text{Ar}]4s^2$). The first transition metal, *scandium*, has one electron in the $3d$ orbitals; the second, *titanium*, has two; and the third, *vanadium*, has three. We would expect *chromium*, the fourth transition metal, to have the electron configuration $[\text{Ar}]4s^23d^4$. However, the actual configuration is $[\text{Ar}]4s^13d^5$, which shows a half-filled $4s$ orbital and a half-filled set of $3d$ orbitals (one electron in each of the five $3d$ orbitals). It is tempting to say that the configuration results because half-filled “shells” are especially stable. Although there are some reasons to think that this explanation might be valid, it is an oversimplification. For instance, tungsten, which is in the same vertical group as chromium, has the configuration $[\text{Xe}]6s^24f^{14}5d^4$, where half-filled s and d shells are not found. There are several similar cases.

Basically, the chromium configuration occurs because the energies of the $3d$ and $4s$ orbitals are very similar for the first-row transition elements. We saw in Section 7.11 that when electrons are placed in a set of degenerate orbitals, they first occupy each orbital singly to minimize electron repulsions. Since the $4s$ and $3d$ orbitals are virtually degenerate in the chromium atom, we would expect the configuration



rather than



TABLE 21.2 Selected Properties of the First-Row Transition Metals

	Scandium	Titanium	Vanadium	Chromium	Manganese	Iron	Cobalt	Nickel	Copper	Zinc
Atomic number	21	22	23	24	25	26	27	28	29	30
Electron configuration*	$4s^23d^1$	$4s^23d^2$	$4s^23d^3$	$4s^13d^5$	$4s^23d^5$	$4s^23d^6$	$4s^23d^7$	$4s^23d^8$	$4s^13d^{10}$	$4s^23d^{10}$
Atomic radius (pm)	162	147	134	130	135	126	125	124	128	138
Ionization energies (eV/atom)										
First	6.54	6.82	6.74	6.77	7.44	7.87	7.86	7.64	7.73	9.39
Second	12.80	13.58	14.65	16.50	15.64	16.18	17.06	18.17	20.29	17.96
Third	24.76	27.49	29.31	30.96	33.67	30.65	33.50	35.17	36.83	39.72
Reduction potential† (V)	-2.08	-1.63	-1.2	-0.91	-1.18	-0.44	-0.28	-0.23	+0.34	-0.76
Common oxidation states	+3	+2, +3, +4	+2, +3, +4, +5	+2, +3, +6	+2, +3, +4, +7	+2, +3	+2, +3	+2	+1, +2	+2
Melting point (°C)	1397	1672	1710	1900	1244	1530	1495	1455	1083	419
Density (g/cm ³)	2.99	4.49	5.96	7.20	7.43	7.86	8.9	8.90	8.92	7.14
Electrical conductivity‡	—	2	3	10	2	17	24	24	97	27

* Each atom has an argon inner-core configuration.

† For the reduction process $M^{2+} + 2e^- \rightarrow M$ (except for scandium, where the ion is Sc^{3+}).

‡ Compared with an arbitrarily assigned value of 100 for silver.

Copper has the electron configuration $[Ar]4s^13d^{10}$.

In transition metal ions, the $3d$ orbitals are lower in energy than the $4s$ orbitals.

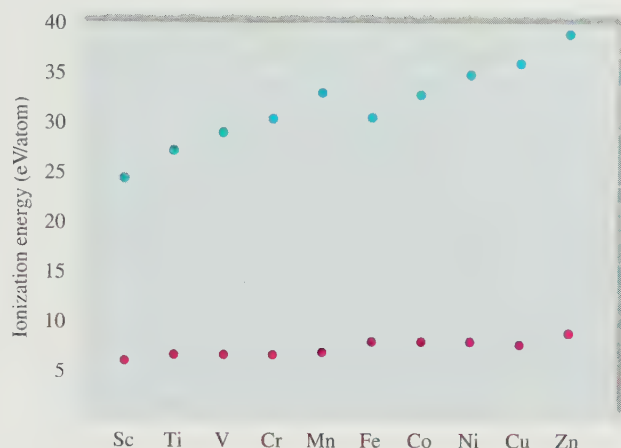
since the second arrangement has greater electron–electron repulsions and thus a higher energy.

The only other unexpected configuration among the first-row transition metals is that of copper, which is $[Ar]4s^13d^{10}$ rather than the expected $[Ar]4s^23d^9$.

In contrast to the neutral transition metals, where the $3d$ and $4s$ orbitals have very similar energies, the *energy of the $3d$ orbitals in transition metal ions is significantly less than that of the $4s$ orbital*. This means that the electrons remaining after the ion is formed occupy the $3d$ orbitals, since they are lower in energy. *First-row transition metal ions do not have $4s$ electrons*. For example, manganese has the configuration $[Ar]4s^23d^5$, while that of Mn^{2+} is $[Ar]3d^5$. The neutral titanium atom has the configuration $[Ar]4s^23d^2$, while that of Ti^{3+} is $[Ar]3d^1$.

Oxidation States and Ionization Energies

The transition metals can form a variety of ions by losing one or more electrons. The common oxidation states of these elements are shown in Table 21.2. Note that for the first five metals the maximum possible oxidation state corresponds to the loss of all the $4s$ and $3d$ electrons. For example, the maximum oxidation state of chromium ($[Ar]4s^13d^5$) is +6. Toward the right end of the period, the maximum oxidation states are not observed; in fact, the $2+$ ions are the most common. The higher oxidation states are not seen for these metals because the $3d$ orbitals become

**FIGURE 21.2**

Plots of the first (red dots) and third (blue dots) ionization energies for the first-row transition metals.

lower in energy as the nuclear charge increases, and the electrons become increasingly difficult to remove. From Table 21.2 we see that ionization energy increases gradually going from left to right across the period. However, the third ionization energy (when an electron is removed from a 3d orbital) increases faster than the first ionization energy, clear evidence of the significant decrease in the energy of the 3d orbitals going across the period (see Fig. 21.2).

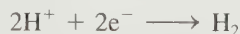
Standard Reduction Potentials

When a metal acts as a *reducing agent*, the half-reaction is



This is the reverse of the conventional listing for half-reactions in tables. Thus, to rank the transition metals in order of reducing ability, it is most convenient to reverse the reactions and the signs given in Table 21.2. The metal with the most positive potential is then the best reducing agent. The transition metals are listed in order of reducing ability in Table 21.3.

Since $\mathcal{E}^{\circ}$ is zero for the process



all the metals except copper can reduce H^{+} ions to hydrogen gas in 1 M aqueous solutions of strong acid:



As Table 21.3 shows, the reducing abilities of the first-row transition metals generally decrease going from left to right across the period. Only chromium and zinc do not follow this trend.

The 4d and 5d Transition Series

In comparing the 3d, 4d, and 5d transition series, it is instructive to consider the atomic radii of these elements (Fig. 21.3). Note that there is a general, although not regular, decrease in size going from left to right for each of the series. Also note that although there is a significant increase in radius in going from the 3d to the 4d metals, the 4d and 5d metals are remarkably similar in size. This latter phenome-

TABLE 21.3

Relative Reducing Abilities of the First-Row Transition Metals in Aqueous Solution

Reaction	Potential (V)
Sc $\rightarrow$ Sc ³⁺ + 3e ⁻	2.08
Ti $\rightarrow$ Ti ²⁺ + 2e ⁻	1.63
V $\rightarrow$ V ²⁺ + 2e ⁻	1.2
Mn $\rightarrow$ Mn ²⁺ + 2e ⁻	1.18
Cr $\rightarrow$ Cr ²⁺ + 2e ⁻	0.91
Zn $\rightarrow$ Zn ²⁺ + 2e ⁻	0.76
Fe $\rightarrow$ Fe ²⁺ + 2e ⁻	0.44
Co $\rightarrow$ Co ²⁺ + 2e ⁻	0.28
Ni $\rightarrow$ Ni ²⁺ + 2e ⁻	0.23
Cu $\rightarrow$ Cu ²⁺ + 2e ⁻	-0.34

Reducing ability ↑

non is the result of the **lanthanide contraction**. In the **lanthanide series**, consisting of the elements between lanthanum and hafnium (see Fig. 21.1), electrons are filling the $4f$ orbitals. Since the $4f$ orbitals are buried in the interior of these atoms, the additional electrons do not add to the atomic size. In fact, the increasing nuclear charge (remember that a proton is added to the nucleus for each electron) causes the radii of the lanthanide elements to decrease significantly going from left to right. This lanthanide contraction just offsets the normal increase in size due to going from one principal quantum level to another. Thus the $5d$ elements, instead of being significantly larger than the $4d$ elements, are almost identical to them in size. This leads to a great similarity in the chemistry of the $4d$ and $5d$ elements in a given vertical group. For example, the chemical properties of hafnium and zirconium are remarkably similar, and they always occur together in nature. Their separation, which is probably more difficult than the separation of any other pair of elements, often requires fractional distillation of their compounds.

In general, the differences between the $4d$ and $5d$ elements in a group increase gradually going from left to right. For example, niobium and tantalum are also quite similar, but less so than zirconium and hafnium.

Although generally less well known than the $3d$ elements, the $4d$ and $5d$ transition metals have certain very useful properties. For example, zirconium and zirconium oxide (ZrO_2) have great resistance to high temperatures and are used, along with niobium and molybdenum alloys, for space vehicle parts that are exposed to high temperatures during reentry into the earth's atmosphere. Niobium and molybdenum are also important alloying materials for certain types of steel. Tantalum, which has a high resistance to attack by body fluids, is often used for replacement of bones. The *platinum group metals*—ruthenium, osmium, rhodium, iridium, palladium, and platinum—are all quite similar and are widely used as catalysts for many types of industrial processes.

Niobium was originally called *columbium* and is still occasionally referred to by that name.

21.2 The First-Row Transition Metals

We have seen that the transition metals are similar in many ways but also show important differences. We will now explore some of the specific properties of each of the $3d$ transition metals.

Scandium is a rare element that exists in compounds mainly in the $+3$ oxidation state, for example, in ScCl_3 , Sc_2O_3 , and $\text{Sc}_2(\text{SO}_4)_3$. The chemistry of scandium

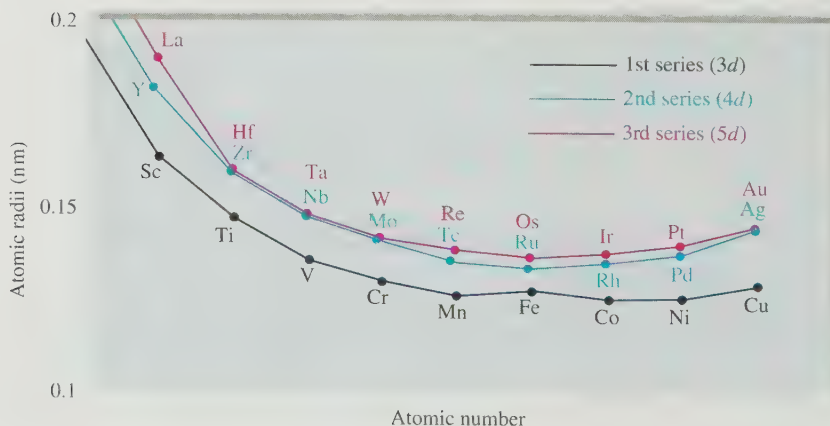
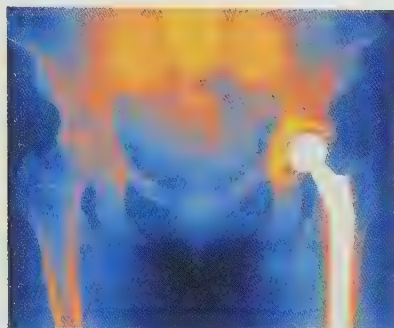


FIGURE 21.3
Atomic radii of the $3d$, $4d$, and $5d$ transition series.



An X ray of a patient who has had a hip replacement. The normal hip joint is on the left; the hip joint constructed from tantalum metal is on the right.



$\text{Ti}(\text{H}_2\text{O})_6^{3+}$ is purple in solution.

The manufacture of sulfuric acid was discussed at the end of Chapter 3.

The most common oxidation state for vanadium is +5.

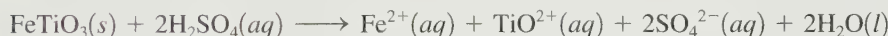
strongly resembles that of the lanthanides, with most of its compounds being colorless and diamagnetic. This is not surprising; as we will see in Section 21.6, the color and magnetism of transition metal compounds usually arise from the d electrons on the metal ion, and Sc^{3+} has no d electrons. Scandium metal, which can be prepared by electrolysis of molten ScCl_3 , is not widely used because of its rarity, but it is found in some electronic devices, such as high-intensity lamps.

Titanium is widely distributed in the earth's crust (0.6% by mass). Because of its relatively low density and high strength, titanium is an excellent structural material, especially in jet engines, where light weight and stability at high temperatures are required. Nearly 5000 kg of titanium alloys is used in each engine of a Boeing 747 jetliner. In addition, the resistance of titanium to chemical attack makes it a useful material for pipes, pumps, and reaction vessels in the chemical industry.

The most familiar compound of titanium is no doubt responsible for the white color of this paper. Titanium dioxide, or more correctly, *titanium(IV) oxide* (TiO_2), is a highly opaque substance used as the white pigment in paper, paint, linoleum, plastics, synthetic fibers, whitewall tires, and cosmetics (sunscreens, for example). Approximately 700,000 tons is used annually in these and other products. Titanium(IV) oxide is widely dispersed in nature, but the main ores are rutile (impure TiO_2) and ilmenite (FeTiO_3). Rutile is processed by treatment with chlorine to form volatile TiCl_4 , which is separated from the impurities and burned to form TiO_2 :



Ilmenite is treated with sulfuric acid to form a soluble sulfate:



When this aqueous mixture is allowed to stand, under vacuum, solid $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ forms first and is removed. The mixture is then heated, and the insoluble titanium(IV) oxide hydrate ($\text{TiO}_2 \cdot \text{H}_2\text{O}$) forms. The water of hydration is driven off by heating to form pure TiO_2 :



In its compounds, titanium is most often found in the +4 oxidation state. Examples are TiO_2 and TiCl_4 , the latter a colorless liquid (bp = 137°C) that fumes in moist air to produce TiO_2 :



Titanium(III) compounds can be produced by reduction of the +4 state. In aqueous solution, Ti^{3+} exists as the purple $\text{Ti}(\text{H}_2\text{O})_6^{3+}$ ion, which is slowly oxidized to titanium(IV) by air. Titanium(II) is not stable in aqueous solution but does exist in the solid state in compounds such as TiO and the dihalides of general formula TiX_2 .

Vanadium is widely spread throughout the earth's crust (0.02% by mass). It is used mostly in alloys with other metals such as iron (80% of vanadium is used in steel) and titanium. Vanadium(V) oxide (V_2O_5) is used as an industrial catalyst in the production of materials such as sulfuric acid.

Pure vanadium can be obtained from the electrolytic reduction of fused salts, such as VCl_2 , to produce a metal similar to titanium that is steel gray, hard, and corrosion resistant. Often the pure element is not required for alloying. For example, *ferrovanadium*, produced by the reduction of a mixture of V_2O_5 and Fe_2O_3 with aluminum, is added to iron to form *vanadium steel*, a hard steel used for engine parts and axles.

CHEMICAL IMPACT

Titanium Dioxide—Miracle Coating

Titanium dioxide, more properly called titanium(IV) oxide, is a very important material. Approximately 1.5 million tons of the substance is produced each year in the United States for use as a pigment in paper and paints and as a component of sunscreens.

In recent years, however, scientists have found a new use for TiO_2 . When surfaces are coated with titanium dioxide, they become resistant to dirt and bacteria. For example, the Pilkington Glass Company is now making glass coated with TiO_2 that cleans itself. All the glass needs is sun and rain to keep itself clean. The self-cleaning action arises from two effects. First, the coating of TiO_2 acts as a catalyst in the presence of ultraviolet (UV) light to break down carbon-based pollutants to carbon dioxide and water. Second, because TiO_2 reduces surface tension, rainwater “sheets” instead of forming droplets on the glass, thereby washing away the grime on the surface of the glass. Although this self-cleaning glass is bad news for window washers, it could save millions of dollars in maintenance costs for owners of commercial buildings.

Because the TiO_2 -treated glass requires UV light for its action, it does not work well for interior surfaces where UV light is present only in small amounts. However, a team of Japanese researchers has found that if the TiO_2 coating is doped with nitrogen atoms, it will catalyze the breakdown of dirt in the presence of visible light as well as UV light. Studies also show that this N-doped TiO_2 surface coating kills many types of bacteria in the presence of visible or ultraviolet light. This discovery could lead to products such as self-sterilizing bathroom tiles, counters, and toilets. In addition, because the TiO_2 on the surface of glass has such a strong attraction for water molecules (greatly lowering the surface tension), water does not bead up to form droplets. Just as this effect produces sheeting action on exterior glass, so it prevents interior windows and mirrors from “fogging up.”

Titanium dioxide, a cheap and plentiful material, may prove to be worth its weight in gold as a surface coating.

TABLE 21.4
Oxidation States and Species for Vanadium in Aqueous Solution

Oxidation State of Vanadium	Species in Aqueous Solution
+5	VO_2^+ (yellow)
+4	VO^{2+} (blue)
+3	$\text{V}^{3+}(\text{aq})$ (blue-green)
+2	$\text{V}^{2+}(\text{aq})$ (violet)

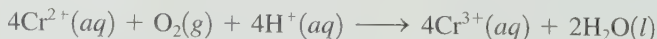
The principal oxidation state of vanadium is +5, found in compounds such as the orange V_2O_5 (mp = 650°C) and the colorless VF_5 (mp = 19.5°C). The oxidation states from +5 to +2 all exist in aqueous solution (see Table 21.4). The higher oxidation states, +5 and +4, do not exist as hydrated ions of the type $\text{V}^{n+}(\text{aq})$ because the highly charged ion causes the attached water molecules to be very acidic. The H^+ ions are lost to give the oxycations VO_2^+ and VO^{2+} . The hydrated V^{3+} and V^{2+} ions are easily oxidized and thus can function as reducing agents in aqueous solution.

Although *chromium* is relatively rare, it is a very important industrial material. The chief ore of chromium is chromite (FeCr_2O_4), which can be reduced by carbon to give *ferrochrome*,



which can be added directly to iron in the steelmaking process. Chromium metal, which is often used to plate steel, is hard and brittle and maintains a bright surface by developing a tough invisible oxide coating.

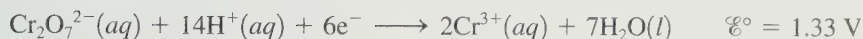
Chromium commonly forms compounds in which it has the oxidation state +2, +3, or +6, as shown in Table 21.5. The Cr^{2+} (chromous) ion is a powerful reducing agent in aqueous solution. In fact, traces of O_2 in other gases can be removed by bubbling through a Cr^{2+} solution:



The chromium(VI) species are excellent oxidizing agents, especially in acidic solution, where chromium(VI) as the dichromate ion ($\text{Cr}_2\text{O}_7^{2-}$) is reduced to the Cr^{3+} ion:

TABLE 21.5
Typical Chromium
Compounds

Oxidation State of Chromium	Examples of Compounds (X = halogen)
+2	CrX ₂
+3	CrX ₃ Cr ₂ O ₃ (green) Cr(OH) ₃ (blue-green)
+6	K ₂ Cr ₂ O ₇ (orange) Na ₂ CrO ₄ (yellow) CrO ₃ (red)

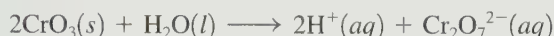


The oxidizing ability of the dichromate ion is strongly pH-dependent, increasing as $[\text{H}^+]$ increases, as predicted by Le Châtelier's principle. In basic solution, chromium(VI) exists as the chromate ion, a much less powerful oxidizing agent:



The structures of the $\text{Cr}_2\text{O}_7^{2-}$ and CrO_4^{2-} ions are shown in Fig. 21.4.

Red chromium(VI) oxide (CrO_3) dissolves in water to give a strongly acidic, red-orange solution:



It is possible to precipitate bright orange dichromate salts, such as $\text{K}_2\text{Cr}_2\text{O}_7$, from these solutions. When made basic, the solution turns yellow, and chromate salts such as Na_2CrO_4 can be obtained. A mixture of chromium(VI) oxide and concentrated sulfuric acid, commonly called *cleaning solution*, is a powerful oxidizing medium that can remove organic materials from analytical glassware, yielding a very clean surface.

Manganese is relatively abundant (0.1% of the earth's crust), although no significant sources are found in the United States. The most common use of manganese is in the production of an especially hard steel used for rock crushers, bank vaults, and armor plate. One interesting source of manganese is from *manganese nodules* found on the ocean floor. These roughly spherical "rocks" contain mixtures of manganese and iron oxides as well as smaller amounts of other metals such as cobalt, nickel, and copper. Apparently, the nodules were formed at least partly by the action of marine organisms. Because of the abundance of these nodules, there is much interest in developing economical methods for their recovery and processing.

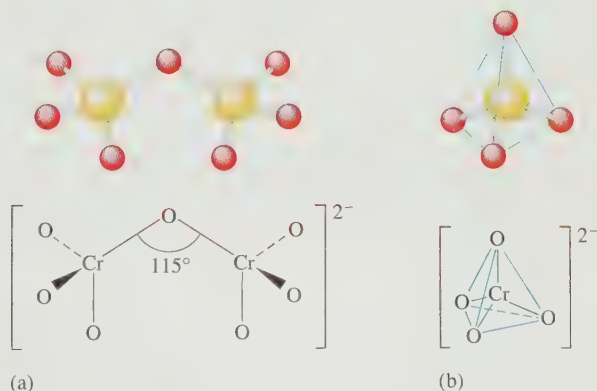
Manganese can exist in all oxidation states from +2 to +7, although +2 and +7 are the most common. Manganese(II) forms an extensive series of salts with all the common anions. In aqueous solution Mn^{2+} forms $\text{Mn}(\text{H}_2\text{O})_6^{2+}$, which has a light pink color. Manganese(VII) is found in the intensely purple permanganate ion (MnO_4^-). Widely used as an analytical reagent in acidic solution, the MnO_4^- ion behaves as a strong oxidizing agent, with the manganese becoming Mn^{2+} :



Several typical compounds of manganese are shown in Table 21.6.

TABLE 21.6
Some Compounds of
Manganese in Its Most
Common Oxidation States

Oxidation State of Manganese	Examples of Compounds
+2	Mn(OH) ₂ (pink) MnS (salmon) MnSO ₄ (reddish) MnCl ₂ (pink)
+4	MnO ₂ (dark brown)
+7	KMnO ₄ (purple)

**FIGURE 21.4**
The structures of the
chromium(VI) anions:
(a) $\text{Cr}_2\text{O}_7^{2-}$, which exists
in acidic solution, and
(b) CrO_4^{2-} , which exists in
basic solution.

Titanium Makes Great Bicycles

One of the most interesting characteristics of the world of bicycling is the competition among various frame materials. Bicycle frames are now built from steel, aluminum, carbon fiber composites, and titanium, with each material having advantages and disadvantages. Steel is strong, economical, adaptable, and (unfortunately) “rustable.” Aluminum is light and stiff but has relatively low fatigue limits (resistance to repeated stresses). Carbon fiber composites have amazing strength-to-mass ratios and have shock- and vibration-dampening properties superior to any metal; however, they are very expensive. Titanium has a density approximately 43% less than that of steel, a yield strength (when alloyed with metals such as aluminum and tin) that is 30% greater than that of steel, an extraordinary resistance to fatigue, and a high resistance to corrosion, but it is expensive and difficult to work.

Of all these materials, titanium gives the bicycle that fanatics seem to love the most. After their first ride on a bicycle with a titanium frame, most experienced cyclists find themselves shaking their heads and searching hard for the right words to describe the experience. Typically, the word “magic” is used a great deal in the ensuing description.

The magic of titanium results from its combination of toughness, stretchability, and resilience. A bicycle that is built stiff to resist pedaling loads usually responds by giving a harsh, uncomfortable ride. A titanium bike is very stiff against high pedaling torques, but it seems to transmit much less road shock than bikes made of competitive materials. Why titanium excels in dampening vibrations is not entirely clear. Despite titanium’s significantly lower density than steel, shock waves travel more slowly in titanium than in steel. Whatever the explanation for its shock-absorbing abilities, titanium provides three things that cyclists find crucial: light weight, stiffness, and a smooth ride—magic.

Titanium is quite abundant in the earth’s crust, ranking ninth of all the elements and second among the transition elements. The metallurgy of titanium presents special challenges. Carbon, the reducing agent most commonly used to obtain metals from their oxide ores, cannot be used because it forms intractable interstitial carbides with titanium. These carbides are extraordinarily hard and have melting points close to 3000°C. However, if chlorine gas is used in



A titanium bicycle.

conjunction with carbon to treat the ore, volatile TiCl_4 is formed, which can be distilled off and then reduced with magnesium or sodium at approximately 1000°C to form a titanium “sponge.” This sponge is then ground up, cleaned with aqua regia (a 1:3 mixture of concentrated HNO_3 and concentrated HCl), melted under a blanket of inert gas (to prevent reaction with oxygen), and cast into ingots. Titanium, a lustrous, silvery metal with a high melting point (1667°C), crystallizes in a hexagonal closest packed structure. Because titanium tends to become quite brittle when trace impurities such as C, N, and O are present, it must be fabricated with great care.

Titanium’s unusual ability to stretch makes it hard to machine. It tends to push away even from a very sharp cutting blade, giving a rather unpredictable final dimension. Also, because titanium is embrittled by reaction with oxygen, all welding operations must be carried out under a shielding gas such as argon.

However, the bicycle that results is worth all these difficulties. One woman described a titanium bicycle as “the one God rides on Sunday.”

Iron is the most abundant heavy metal (4.7% of the earth’s crust) and the most important to our civilization. It is a white, lustrous, not particularly hard metal that is very reactive toward oxidizing agents. For example, in moist air it is rapidly oxidized by oxygen to form rust, a mixture of iron oxides.

TABLE 21.7
Typical Compounds of Iron

Oxidation State of Iron	Examples of Compounds
+2	FeO (black) FeS (brownish black) FeSO ₄ · 7H ₂ O (green) K ₄ Fe(CN) ₆ (yellow)
+3	FeCl ₃ (brownish black) Fe ₂ O ₃ (reddish brown) K ₃ Fe(CN) ₆ (red) Fe(SCN) ₃ (red)
+2, +3 (mixture)	Fe ₃ O ₄ (black) KFe[Fe(CN) ₆] (deep blue, "Prussian blue")

The chemistry of iron mainly involves its +2 and +3 oxidation states. Typical compounds are shown in Table 21.7. In aqueous solutions iron(II) salts are generally light green because of the presence of $\text{Fe}(\text{H}_2\text{O})_6^{2+}$. Although the $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ ion is colorless, aqueous solutions of iron(III) salts are usually yellow to brown in color due to the presence of $\text{Fe}(\text{OH})(\text{H}_2\text{O})_5^{2+}$, which results from the acidity of $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ ($K_a = 6 \times 10^{-3}$):



Although *cobalt* is relatively rare, it is found in ores such as smaltite (CoAs_2) and cobaltite (CoAsS) in large enough concentrations to make its production economically feasible. Cobalt is a hard, bluish white metal mainly used in alloys such as stainless steel and stellite, an alloy of iron, copper, and tungsten that is used in surgical instruments.

The chemistry of cobalt involves mainly its +2 and +3 oxidation states, although compounds containing cobalt in the 0, +1, or +4 oxidation state are known. Aqueous solutions of cobalt(II) salts contain the $\text{Co}(\text{H}_2\text{O})_6^{2+}$ ion, which has a characteristic rose color. Cobalt forms a wide variety of coordination compounds, many of which will be discussed in later sections of this chapter. Some typical cobalt compounds are shown in Table 21.8.

Nickel, which ranks twenty-fourth in elemental abundance in the earth's crust, is found in ores, where it is combined mainly with arsenic, antimony, and sulfur. Nickel metal, a silvery white substance with high electrical and thermal conductivities, is quite resistant to corrosion and is often used for plating more active metals. Nickel is also widely used in the production of alloys such as steel.

Nickel in compounds is almost exclusively in the +2 oxidation state. Aqueous solutions of nickel(II) salts contain the $\text{Ni}(\text{H}_2\text{O})_6^{2+}$ ion, which has a characteristic emerald green color. Coordination compounds of nickel(II) will be discussed later in this chapter. Some typical nickel compounds are shown in Table 21.9.

Copper, widely distributed in nature in ores containing sulfides, arsenides, chlorides, and carbonates, is valued for its high electrical conductivity and its resistance to corrosion. It is widely used for plumbing, and 50% of all copper produced



An aqueous solution containing the Ni^{2+} ion.

TABLE 21.8
Typical Compounds of Cobalt

Oxidation State	Examples of Compounds
+2	CoSO ₄ (dark blue) [Co(H ₂ O) ₆]Cl ₂ (pink) [Co(H ₂ O) ₆](NO ₃) ₂ (red) CoS (black) CoO (greenish brown)
+3	CoF ₃ (brown) Co ₂ O ₃ (charcoal) K ₃ [Co(CN) ₆] (yellow) [Co(NH ₃) ₆]Cl ₃ (yellow)

TABLE 21.9
Typical Compounds of Nickel

Oxidation State of Nickel	Examples of Compounds
+2	NiCl ₂ (yellow) [Ni(H ₂ O) ₆]Cl ₂ (green) NiO (greenish black) NiS (black) [Ni(H ₂ O) ₆]SO ₄ (green) [Ni(NH ₃) ₆](NO ₃) ₂ (blue)

TABLE 21.10 Alloys Containing Copper

Alloy	Composition (% by mass in parentheses)
Brass	Cu (20–97), Zn (2–80), Sn (0–14), Pb (0–12), Mn (0–25)
Bronze	Cu (50–98), Sn (0–35), Zn (0–29), Pb (0–50), P (0–3)
Sterling silver	Cu (7.5), Ag (92.5)
Gold (18-karat)	Cu (5–15), Au (75), Ag (10–20)
Gold (14-karat)	Cu (12–28), Au (58), Ag (4–30)

Copper roofs and bronze statues, such as the Statue of Liberty, turn green in air because $\text{Cu}_3(\text{OH})_4\text{SO}_4$ and $\text{Cu}_4(\text{OH})_6\text{SO}_4$ form.

TABLE 21.11**Typical Compounds of Copper**

Oxidation State of Copper	Examples of Compounds
+1	Cu_2O (red) Cu_2S (black) CuCl (white)
+2	CuO (black) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (blue) $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (green) $[\text{Cu}(\text{H}_2\text{O})_6](\text{NO}_3)_2$ (blue)

annually is used for electrical applications. Copper is a major constituent in several well-known alloys (see Table 21.10).

Although copper is not highly reactive (it will not reduce H^+ to H_2 , for example), the reddish metal does slowly corrode in air, producing the characteristic green *patina* consisting of basic copper sulfate



and other similar compounds.

The chemistry of copper principally involves the +2 oxidation state, but many compounds containing copper(I) are also known. Aqueous solutions of copper(II) salts are a characteristic bright blue color due to the presence of the $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ ion. Table 21.11 lists some typical copper compounds.

Although trace amounts of copper are essential for life, copper in large amounts is quite toxic; copper salts are used to kill bacteria, fungi, and algae. For example, paints containing copper are used on ship hulls to prevent fouling by marine organisms.

Widely dispersed in the earth's crust, *zinc* is mainly refined from sphalerite (ZnS), which often occurs with galena (PbS). Zinc is a white, lustrous, very active metal that behaves as an excellent reducing agent and tarnishes rapidly. About 90% of the zinc produced is used for galvanizing steel. Zinc forms colorless salts in the +2 oxidation state.

21.3 Coordination Compounds

Transition metal ions characteristically form coordination compounds, which are usually colored and often paramagnetic. A **coordination compound** typically consists of a *complex ion*, a transition metal ion with its attached ligands (see Section 15.8), and **counterions**, anions or cations as needed to produce a compound with no net charge. The substance $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ is a typical coordination compound. The brackets indicate the composition of the complex ion, in this case $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$, and the two Cl^- counterions are shown outside the brackets. Note that in this compound one Cl^- acts as a ligand along with the five NH_3 molecules. In the solid state this compound consists of the large $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ cations and twice as many Cl^- anions, all packed together as efficiently as possible. When dissolved in water, the solid behaves like any ionic solid; the cations and anions are assumed to separate and move about independently:

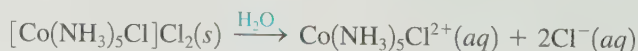


TABLE 21.12 Typical Coordination Numbers for Some Common Metal Ions

M^+	Coordination Numbers	M^{2+}	Coordination Numbers	M^{3+}	Coordination Numbers
Cu^+	2, 4	Mn^{2+}	4, 6	Sc^{3+}	6
Ag^+	2	Fe^{2+}	6	Cr^{3+}	6
Au^+	2, 4	Co^{2+}	4, 6	Co^{3+}	6
		Ni^{2+}	4, 6		
		Cu^{2+}	4, 6	Au^{3+}	4
		Zn^{2+}	4, 6		

Coordination compounds have been known since about 1700, but their true nature was not understood until the 1890s when a young Swiss chemist named Alfred Werner (1866–1919) proposed that transition metal ions have two types of valence (combining ability). One type of valence, which Werner called the *secondary valence*, refers to the ability of a metal ion to bind to Lewis bases (ligands) to form complex ions. The other type, the *primary valence*, refers to the ability of the metal ion to form ionic bonds with oppositely charged ions. Thus Werner explained that the compound, originally written as $CoCl_3 \cdot 5NH_3$, was really $[Co(NH_3)_5Cl]Cl_2$, where the Co^{3+} ion has a primary valence of 3, satisfied by the three Cl^- ions, and a secondary valence of 6, satisfied by the six ligands (five NH_3 and one Cl^-). We now call the primary valence the **oxidation state** and the secondary valence the **coordination number**, which reflects the number of bonds formed between the metal ion and the ligands in the complex ion.

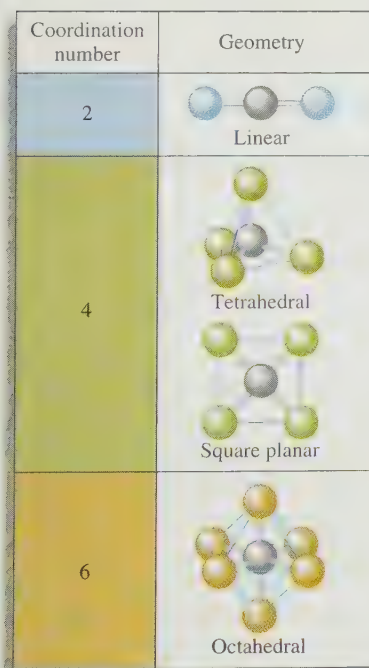


FIGURE 21.5
The ligand arrangements for coordination numbers 2, 4, and 6.

Coordination Number

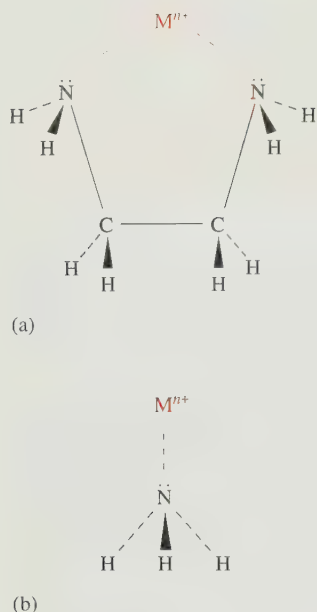
The number of bonds formed by metal ions to ligands in complex ions varies from two to eight depending on the size, charge, and electron configuration of the transition metal ion. As shown in Table 21.12, 6 is the most common coordination number, followed closely by 4, with a few metal ions showing a coordination number of 2. Many metal ions show more than one coordination number, and there is really no simple way to predict what the coordination number will be in a particular case. The typical geometries for the various common coordination numbers are shown in Fig. 21.5. Note that six ligands produce an octahedral arrangement around the metal ion. Four ligands can form either a tetrahedral or a square planar arrangement, and two ligands give a linear structure.

Ligands

A **ligand** is a neutral molecule or ion having a lone electron pair that can be used to form a bond to a metal ion. The formation of a metal–ligand bond therefore can be described as the interaction between a Lewis base (the ligand) and a Lewis acid (the metal ion). The resulting bond is often called a **coordinate covalent bond**.

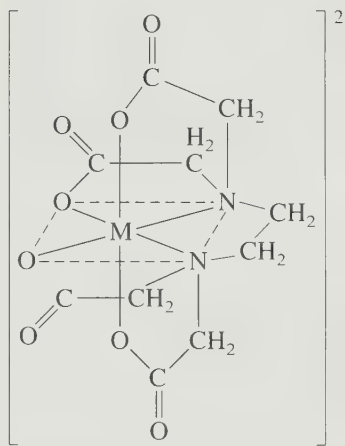
A ligand that can form one bond to a metal ion is called a **monodentate ligand**, or a **unidentate ligand** (from root words meaning “one tooth”). Examples of unidentate ligands are shown in Table 21.13.

Some ligands have more than one atom with a lone electron pair that can be used to bond to a metal ion. Such ligands are said to be **chelating ligands**, or **chelates**

**FIGURE 21.6**

(a) The bidentate ligand ethylenediamine can bond to the metal ion through the lone pair on each nitrogen atom, thus forming two coordinate covalent bonds.

(b) Ammonia is a monodentate ligand.

**FIGURE 21.7**

The coordination of EDTA with a 2+ metal ion.

TABLE 21.13 Some Common Ligands

Type	Examples	
Unidentate/monodentate	H_2O NH_3	CN^- NO_2^- (nitrite) SCN^- (thiocyanate) X^- (halides) OH^-
Bidentate	Oxalate 	Ethylenediamine (en)
Polydentate	Diethylenetriamine (dien) 	Ethylenediaminetetraacetate (EDTA)

(from the Greek word *chele* for “claw”). A ligand that can form two bonds to a metal ion is called a **bidentate ligand**. A very common bidentate ligand is ethylenediamine (abbreviated en), which is shown coordinating to a metal ion in Fig. 21.6(a). Note the relationship between this ligand and the unidentate ligand ammonia [Fig. 21.6(b)]. Oxalate, another typical bidentate ligand, is shown in Table 21.13.

Ligands that can form more than two bonds to a metal ion are called **polydentate ligands**. Some ligands can form as many as six bonds to a metal ion. The best known example is ethylenediaminetetraacetate (abbreviated EDTA), which is shown in Table 21.13. This ligand virtually surrounds the metal ion (Fig. 21.7), coordinating through six atoms (a **hexadentate ligand**). As might be expected from the large number of coordination sites, EDTA forms very stable complex ions with most metal ions and is used as a “scavenger” to remove toxic heavy metals such as lead from the human body. It is also used as a reagent to analyze solutions for their metal ion content. EDTA is found in countless consumer products, such as soda, beer, salad dressings, bar soaps, and most cleaners. In these products EDTA ties up trace metal ions that would otherwise catalyze decomposition and produce unwanted precipitates.

Some even more complicated ligands are found in biologic systems, where metal ions play crucial roles in catalyzing reactions, transferring electrons, and transporting and storing oxygen. A discussion of these complex ligands will follow in Section 21.7.

TABLE 21.14
Names of Some Common
Unidentate Ligands

Neutral Molecules	
Aqua	H ₂ O
Ammine	NH ₃
Methylamine	CH ₃ NH ₂
Carbonyl	CO
Nitrosyl	NO
Anions	
Fluoro	F ⁻
Chloro	Cl ⁻
Bromo	Br ⁻
Iodo	I ⁻
Hydroxo	OH ⁻
Cyano	CN ⁻

Nomenclature

In Werner's lifetime, no system was used to name coordination compounds. Names of the compounds were commonly based on colors and names of discoverers. As the field expanded and more coordination compounds were identified, an orderly system of nomenclature became necessary. A simplified version of this system is summarized by the following rules.

Rules for Naming Coordination Compounds

- As with any ionic compound, the *cation is named before the anion*.
- In naming a complex ion, the *ligands are named before the metal ion*.
- In naming ligands, an *o* is added to the root name of an anion. For example, the halides as ligands are called *fluoro*, *chloro*, *bromo*, and *iodo*; hydroxide is *hydroxo*; cyanide is *cyano*; etc. For a neutral ligand the name of the molecule is used, with the exception of H₂O, NH₃, CO, and NO, as illustrated in Table 21.14.
- The prefixes *mono-*, *di-*, *tri-*, *tetra-*, *penta-*, and *hexa-* are used to denote the number of simple ligands. The prefixes *bis-*, *tris-*, *tetrakis-*, and so on are also used, especially for more complicated ligands or ones that already contain *di-*, *tri-*, etc.
- The oxidation state of the central metal ion is designated by a Roman numeral in parentheses.
- When more than one type of ligand is present, they are named alphabetically.* Prefixes do not affect the order.
- If the complex ion has a negative charge, the suffix *-ate* is added to the name of the metal. Sometimes the Latin name is used to identify the metal (see Table 21.15).

The application of these rules is shown in Sample Exercise 21.1.

SAMPLE EXERCISE 21.1

Naming Coordination Compounds I

Give the systematic name for each of the following coordination compounds.

- a. [Co(NH₃)₃Cl]Cl₂
- b. K₃Fe(CN)₆
- c. [Fe(en)₂(NO₂)₂]₂SO₄

SOLUTION

- a. To determine the oxidation state of the metal ion, we examine the charges of all ligands and counterions. The ammonia molecules are neutral and each of the chloride ions has a 1⁻ charge, so the cobalt ion must have a 3⁺ charge to produce a neutral compound. Thus cobalt has the oxidation state +3, and we use cobalt(III) in the name.

The ligands include one Cl⁻ ion and five NH₃ molecules. The chloride ion is designated as *chloro*, and each ammonia molecule is designated as *ammine*. The prefix *penta-* indicates that there are five NH₃ ligands present. The name of the

TABLE 21.15
Latin Names Used for Some
Metal Ions in Anionic
Complex Ions

Metal	Name in an Anionic Complex
Iron	Ferrate
Copper	Cuprate
Lead	Plumbate
Silver	Argentate
Gold	Aurate
Tin	Stannate

* In an older system the negatively charged ligands were named first, then neutral ligands, with positively charged ligands named last. We will follow the newer convention in this text.

complex cation is therefore pentaamminechlorocobalt(III). Note that the ligands are named alphabetically, disregarding the prefix. Since the counterions are chloride ions, the compound is named as a chloride salt:



(top) An aqueous solution of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$. (bottom) Solid $\text{K}_3\text{Fe}(\text{CN})_6$.

- b. First, we determine the oxidation state of the iron by considering the other charged species. The compound contains three K^+ ions and six CN^- ions. Therefore, the iron must carry a charge of 3+, giving a total of six positive charges to balance the six negative charges. The complex ion present is thus $\text{Fe}(\text{CN})_6^{3-}$. The cyanide ligands are each designated *cyano*, and the prefix *hexa-* indicates that six are present. Since the complex ion is an anion, we use the Latin name *ferrate*. The oxidation state is indicated by (III) at the end of the name. The anion name is therefore hexacyanoferrate(III). The cations are K^+ ions, which are simply named potassium. Putting this together gives the name



(The common name of this compound is potassium ferricyanide.)

- c. We first determine the oxidation state of the iron by looking at the other charged species: four NO_2^- ions and one SO_4^{2-} ion. The ethylenediamine is neutral. Thus the two iron ions must carry a total positive charge of 6 to balance the six negative charges. This means that each iron has a +3 oxidation state and is designated as iron(III).

Since the name ethylenediamine already contains *di*, we use *bis-* instead of *di-* to indicate the two en ligands. The name for NO_2^- as a ligand is *nitro*, and the prefix *di-* indicates the presence of two NO_2^- ligands. Since the anion is sulfate, the compound's name is



Because the complex ion is a cation, the Latin name for iron is not used.

See Exercises 21.29 through 21.32.

SAMPLE EXERCISE 21.2

Naming Coordination Compounds II

Given the following systematic names, give the formula of each coordination compound.

- Triaminebromoplatinum(II) chloride
- Potassium hexafluorocobaltate(III)

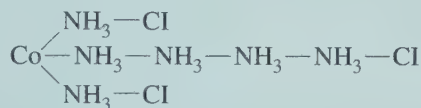
SOLUTION

- a. *Triamine* signifies three ammonia ligands, and *bromo* indicates one bromide ion as a ligand. The oxidation state of platinum is +2, as indicated by the Roman numeral II. Thus the complex ion is $[\text{Pt}(\text{NH}_3)_3\text{Br}]^+$. One chloride ion is needed to balance the 1+ charge of this cation. The formula of the compound is $[\text{Pt}(\text{NH}_3)_3\text{Br}]\text{Cl}$. Note that brackets enclose the complex ion.

CHEMICAL IMPACT

Alfred Werner: Coordination Chemist

During the early and middle parts of the nineteenth century, chemists prepared a large number of colored compounds containing transition metals and other substances such as ammonia, chloride ion, cyanide ion, and water. These compounds were very interesting to chemists who were trying to understand the nature of bonding (Dalton's atomic theory of 1808 was very new at this time), and many theories were suggested to explain these substances. The most widely accepted early theory was the *chain theory*, championed by Sophus Mads Jorgensen (1837–1914), professor of chemistry at the University of Copenhagen. The chain theory got its name from the postulate that metal ammine* complexes contain chains of NH_3 molecules. For example, Jorgensen proposed the structure



for the compound $\text{Co}(\text{NH}_3)_6\text{Cl}_3$. In the late nineteenth century this theory was used in classrooms around the world to explain the nature of metal–ammine compounds.

However, in 1890, a young Swiss chemist named Alfred Werner, who had just obtained a Ph.D. in the field of organic chemistry, became so interested in these compounds that he apparently even dreamed about them. In the middle of one night Werner awoke realizing that he had the correct

*Ammine is the name for NH_3 as a ligand.

explanation for the constitution of these compounds. Writing furiously the rest of that night and into the late afternoon of the following day, he constructed a scientific paper containing his now famous *coordination theory*. This model postulates an octahedral arrangement of ligands around the Co^{3+} ion, producing the $\text{Co}(\text{NH}_3)_6^{3+}$ complex ion with three Cl^- ions as counterions. Thus Werner's picture of $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ varied greatly from the chain theory.

In his paper on the coordination theory, Werner explained not only the metal–ammine compounds but also most of the other known transition metal compounds, and the importance of his contribution was recognized immediately. He was appointed professor at the University of Zurich, where he spent the rest of his life studying coordination compounds and refining his theory. Alfred Werner was a confident, impulsive man of seemingly boundless energy, who was known for his inspiring lectures, his intolerance of incompetence (he once threw a chair at a student who performed poorly on an oral exam), and his intuitive scientific brilliance. For example, he was the first to show that stereochemistry is a general phenomenon, not one exhibited only by carbon, as was previously thought. He also recognized and named many types of isomerism.

In 1913, for his work on coordination chemistry and stereochemistry, Werner became the fourteenth Nobel Prize winner in chemistry and the first Swiss chemist to be so honored. Werner's work is even more remarkable when one realizes that his ideas preceded by many years any real understanding of the nature of covalent bonds.

- b. The complex ion contains six fluoride ligands attached to a Co^{3+} ion to give CoF_6^{3-} . Note that the *-ate* ending indicates that the complex ion is an anion. The cations are K^+ ions, and three are required to balance the 3– charge on the complex ion. Thus the formula is $\text{K}_3[\text{CoF}_6]$.

See Exercises 21.33 and 21.34.

21.4 Isomerism

When two or more species have the same formula but different properties, they are said to be **isomers**. Although isomers contain exactly the same types and numbers of atoms, the arrangements of the atoms differ, and this leads to different properties. We will consider two main types of isomerism: **structural isomerism**, where the isomers contain the same atoms but one or more bonds differ, and **stereoisomerism**,

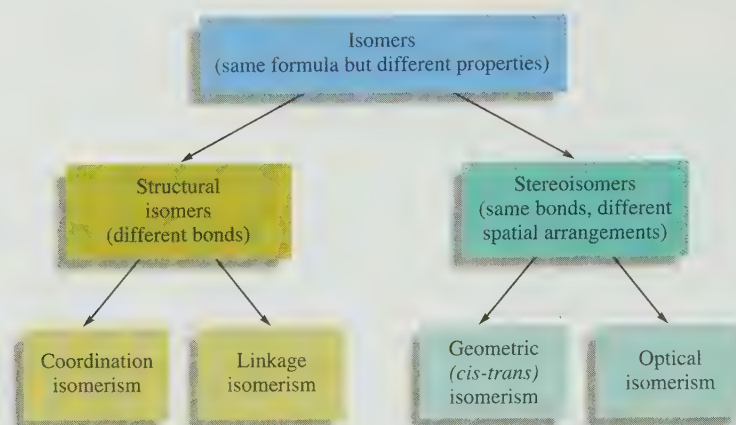


FIGURE 21.8
Some classes of isomers.

where all the bonds in the isomers are the same but the spatial arrangements of the atoms are different. Each of these classes also has subclasses (see Fig. 21.8), which we will now consider.

Structural Isomerism

The first type of structural isomerism we will consider is **coordination isomerism**, in which the composition of the complex ion varies. For example, $[\text{Cr}(\text{NH}_3)_5\text{SO}_4]\text{Br}$ and $[\text{Cr}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ are coordination isomers. In the first case, SO_4^{2-} is coordinated to Cr^{3+} , and Br^- is the counterion; in the second case, the roles of these ions are reversed.

Another example of coordination isomerism is the $[\text{Co}(\text{en})_3][\text{Cr}(\text{ox})_3]$ and $[\text{Cr}(\text{en})_3][\text{Co}(\text{ox})_3]$ pair, where ox represents the oxalate ion, a bidentate ligand shown in Table 21.13.

In a second type of structural isomerism, **linkage isomerism**, the composition of the complex ion is the same, but the point of attachment of at least one of the ligands differs. Two ligands that can attach to metal ions in different ways are thiocyanate (SCN^-), which can bond through lone electron pairs on the nitrogen or the sulfur atom, and the nitrite ion (NO_2^-), which can bond through lone electron pairs on the nitrogen or the oxygen atom. For example, the following two compounds are linkage isomers:

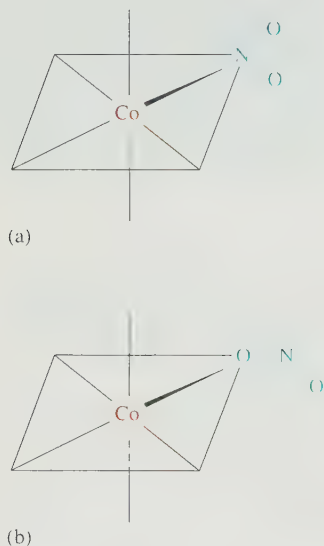
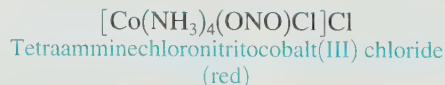
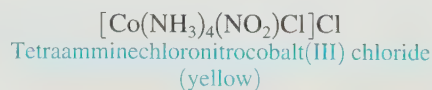


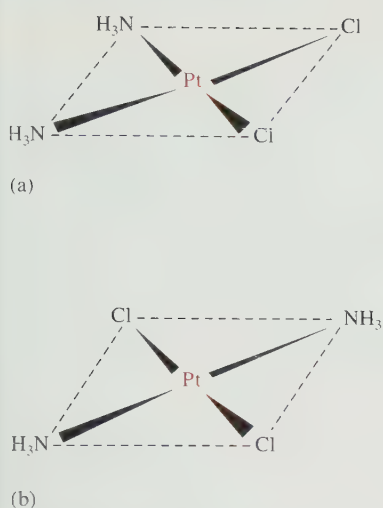
FIGURE 21.9
As a ligand, NO_2^- can bond to a metal ion (a) through a lone pair on the nitrogen atom or (b) through a lone pair on one of the oxygen atoms.



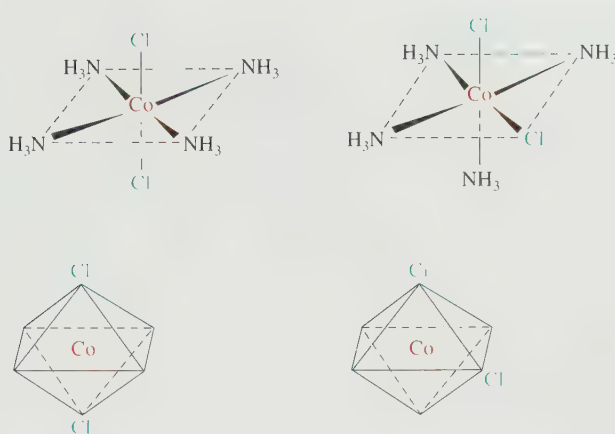
In the first case, the NO_2^- ligand is called *nitro* and is attached to Co^{3+} through the nitrogen atom; in the second case, the NO_2^- ligand is called *nitrito* and is attached to Co^{3+} through an oxygen atom (see Fig. 21.9).

Stereoisomerism

Stereoisomers have the same bonds but different spatial arrangements of the atoms. One type, **geometrical isomerism**, or **cis-trans isomerism**, occurs when atoms or

**FIGURE 21.10**

(a) The *cis* isomer of $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ (yellow). (b) The *trans* isomer of $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ (pale yellow).

**FIGURE 21.11**

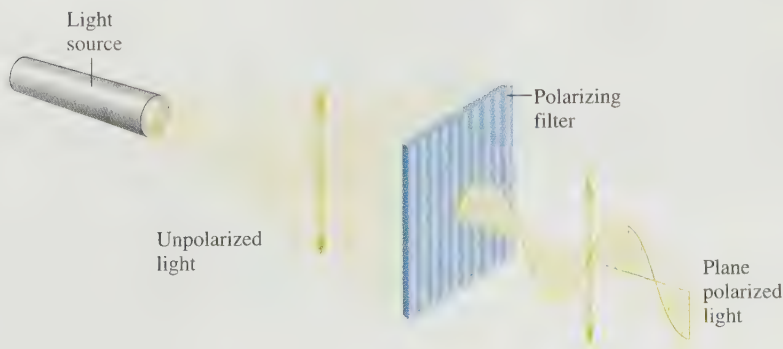
(a) The *trans* isomer of $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$. The chloride ligands are directly across from each other. (b) The *cis* isomer of $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$. The chloride ligands in this case share an edge of the octahedron. Because of their different structures, the *trans* isomer of $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ is green and the *cis* isomer is violet.

groups of atoms can assume different positions around a rigid ring or bond. An important example is the compound $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$, which has a square planar structure. The two possible arrangements of the ligands are shown in Fig. 21.10. In the ***trans* isomer**, the ammonia molecules are across (*trans*) from each other. In the ***cis* isomer**, the ammonia molecules are next (*cis*) to each other.

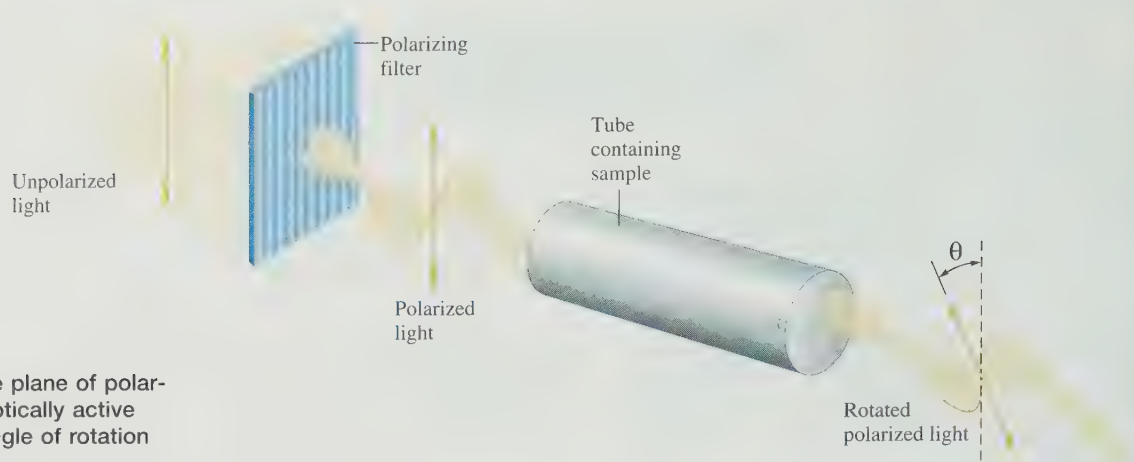
Geometrical isomerism also occurs in octahedral complex ions. For example, the compound $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ has *cis* and *trans* isomers (Fig. 21.11).

A second type of stereoisomerism is called **optical isomerism** because the isomers have opposite effects on plane-polarized light. When light is emitted from a source such as a glowing filament, the oscillating electric fields of the photons in the beam are oriented randomly, as shown in Fig. 21.12. If this light is passed through a polarizer, only the photons with electric fields oscillating in a single plane remain, constituting *plane-polarized light*.

In 1815, a French physicist, Jean Biot (1774–1862), showed that certain crystals could rotate the plane of polarization of light. Later it was found that solutions of certain compounds could do the same thing (see Fig. 21.13). Louis Pasteur (1822–1895) was the first to understand this behavior. In 1848 he noted that solid

**FIGURE 21.12**

Unpolarized light consists of waves vibrating in many different planes (indicated by the arrows). The polarizing filter blocks all waves except those vibrating in a given plane.

**FIGURE 21.13**

The rotation of the plane of polarized light by an optically active substance. The angle of rotation is called theta (θ).

sodium ammonium tartrate ($\text{NaNH}_4\text{C}_4\text{H}_4\text{O}_4$) existed as a mixture of two types of crystals, which he painstakingly separated with tweezers. Separate solutions of these two types of crystals rotated plane-polarized light in exactly opposite directions. This led to a connection between optical activity and molecular structure.

We now realize that optical activity is exhibited by molecules that have *non-superimposable mirror images*. Your hands are nonsuperimposable mirror images (Fig. 21.15). The two hands are related like an object and its mirror image; one hand cannot be turned to make it identical to the other. Many molecules show this same feature, such as the complex ion $[\text{Co}(\text{en})_3]^{3+}$ shown in Fig. 21.16. Objects that have nonsuperimposable mirror images are said to be **chiral** (from the Greek word *cheir*, meaning “hand”).

The isomers of $[\text{Co}(\text{en})_3]^{3+}$ (Fig. 21.17) are nonsuperimposable mirror images called **enantiomers**, which rotate plane-polarized light in opposite directions and are thus optical isomers. The isomer that rotates the plane of light to the right (when viewed down the beam of oncoming light) is said to be *dextrorotatory*, designated by *d*. The isomer that rotates the plane of light to the left is *levorotatory* (*l*). An equal mixture of the *d* and *l* forms in solution, called a *racemic mixture*, does not rotate the plane of the polarized light at all because the two opposite effects cancel each other.

Geometrical isomers are not necessarily optical isomers. For instance, the *trans* isomer of $[\text{Co}(\text{en})_2\text{Cl}_2]^+$ shown in Fig. 21.17 is identical to its mirror image. Since this isomer is superimposable on its mirror image, it does not exhibit optical isomerism and is not chiral. On the other hand, *cis*- $[\text{Co}(\text{en})_2\text{Cl}_2]^+$ is *not* superimposable on its mirror image; a pair of enantiomers exists for this complex ion (the *cis* isomer is chiral).

Most important biomolecules are chiral, and their reactions are highly structure dependent. For example, a drug can have a particular effect because its molecules can bind to chiral molecules in the body. To bind correctly, however, the correct optical isomer of the drug must be administered. Just as the right hand of one person requires the right hand of another to perform a handshake, a given isomer in the body requires a specific isomer of the drug to bind together. Because of this, the syntheses of drugs, which are usually very complicated molecules, must be carried out in a way that produces the correct “handedness,” a requirement that greatly adds to the synthetic difficulties.

CHEMICAL IMPACT

The Importance of Being *cis*

Some of the most important advancements of science are the results of accidental discoveries, for example, penicillin, Teflon, and the sugar substitutes cyclamate and aspartame. Another important chance discovery occurred in 1964, when a group of scientists using platinum electrodes to apply an electric field to a colony of *E. coli* bacteria noticed that the bacteria failed to divide but continued to grow, forming long fibrous cells. Further study revealed that cell division was inhibited by small concentrations of *cis*- $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ and *cis*- $\text{Pt}(\text{NH}_3)_2\text{Cl}_4$ formed electrolytically in the solution.

Cancerous cells multiply very rapidly because cell division is uncontrolled. Thus these and similar platinum complexes were evaluated as *antitumor agents*, which inhibit the division of cancer cells. The results showed that *cis*-

$\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ was active against a wide variety of tumors, including testicular and ovarian tumors, which are very resistant to treatment by more traditional methods. However, although the *cis* complex showed significant antitumor activity, the corresponding *trans* complex had no effect on tumors. This shows the importance of isomerism in biologic systems. When drugs are synthesized, great care must be taken to obtain the correct isomer.

Although *cis*- $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ has proven to be a valuable drug, unfortunately it has some troublesome side effects, the most serious being kidney damage. As a result, the search continues for even more effective antitumor agents. Promising candidates are shown in Fig. 21.14. Note that they are all *cis* complexes.

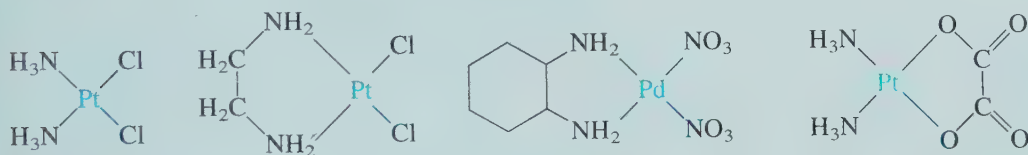


FIGURE 21.14

Some *cis* complexes of platinum and palladium that show significant antitumor activity. It is thought that the *cis* complexes work by losing two adjacent ligands and forming coordinate covalent bonds to adjacent bases on a DNA molecule.

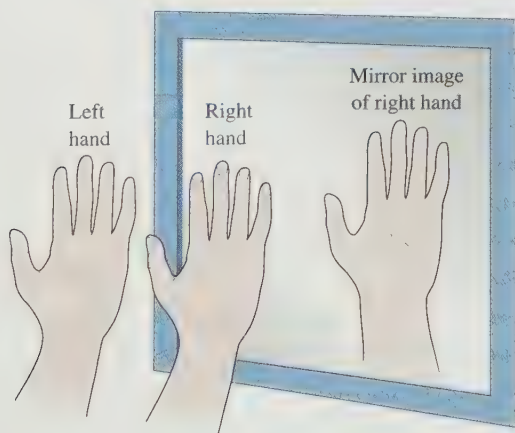
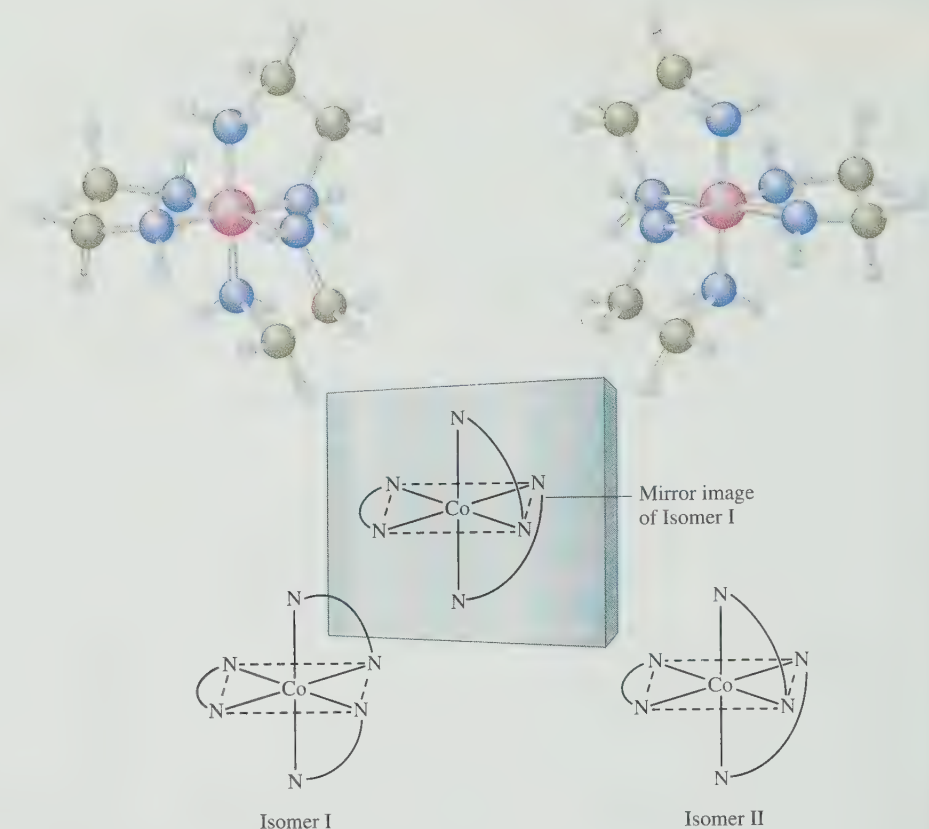
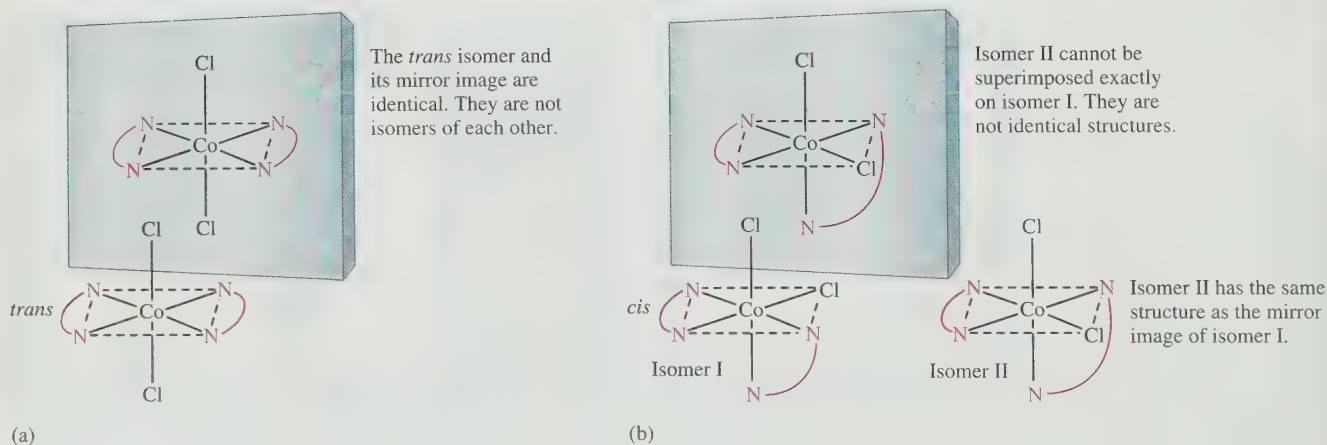


FIGURE 21.15

A human hand exhibits a nonsuperimposable mirror image. Note that the mirror image of the right hand (while identical to the left hand) cannot be turned in any way to make it identical to (superimposable on) the actual right hand.

**FIGURE 21.16**

Isomers I and II of $\text{Co}(\text{en})_3^{3+}$ are mirror images (the image of I is identical to II) that cannot be superimposed. That is, there is no way that I can be turned in space so that it is the same as II.

**FIGURE 21.17**

(a) The *trans* isomer of $\text{Co}(\text{en})_2\text{Cl}_2^+$ and its mirror image are identical (superimposable). (b) The *cis* isomer of $\text{Co}(\text{en})_2\text{Cl}_2^+$ and its mirror image are not superimposable and are thus a pair of optical isomers.

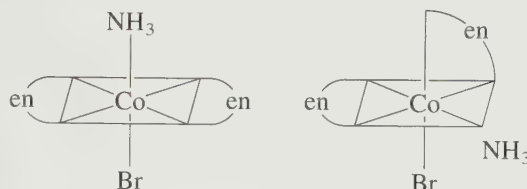
SAMPLE EXERCISE 21.3

Geometrical and Optical Isomerism

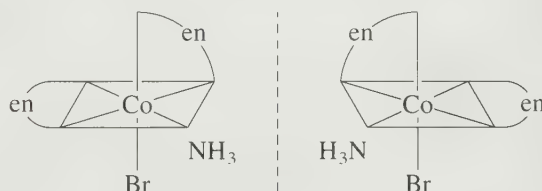
Does the complex ion $[\text{Co}(\text{NH}_3)\text{Br}(\text{en})_2]^{2+}$ exhibit geometrical isomerism? Does it exhibit optical isomerism?

SOLUTION

The complex ion exhibits geometrical isomerism because the ethylenediamine ligands can be across from or next to each other:



The *cis* isomer of the complex ion also exhibits optical isomerism because its mirror images



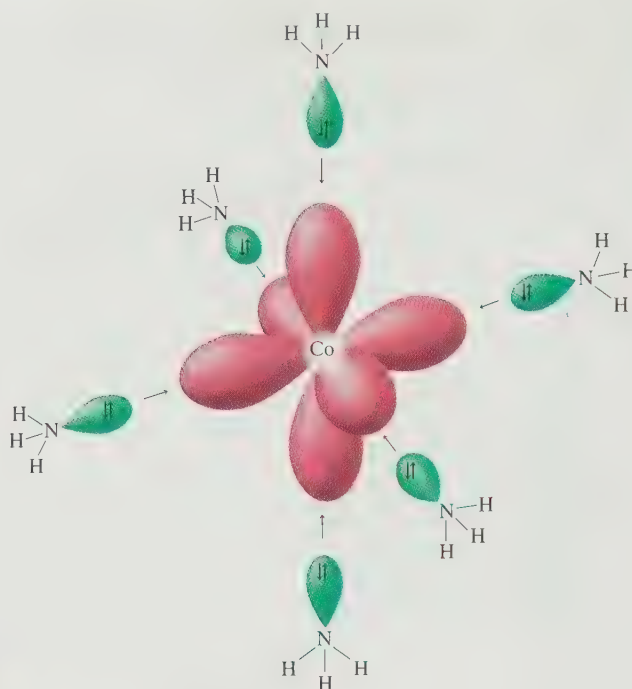
cannot be turned in any way to make them superimposable. Thus these mirror-image isomers of the *cis* complex are shown to be enantiomers that will rotate plane-polarized light in opposite directions.

See Exercises 21.41 and 21.42.

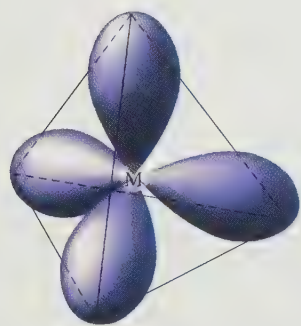
21.5 Bonding in Complex Ions: The Localized Electron Model

In Chapters 8 and 9 we considered the localized electron model, a very useful model for describing the bonding in molecules. Recall that a central feature of this model is the formation of hybrid atomic orbitals that are used to share electron pairs to form σ bonds between atoms. This same model can be used to account for the bonding in complex ions, but there are two important points to keep in mind:

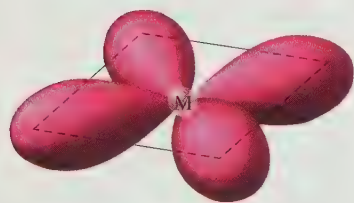
1. The VSEPR model for predicting structure generally *does not work for complex ions*. However, we can safely assume that a complex ion with a coordination number of 6 will have an octahedral arrangement of ligands, and complexes with two ligands will be linear. On the other hand, complex ions with a coordination number of 4 can be either tetrahedral or square planar, and there is no completely reliable way to predict which will occur in a particular case.
2. The interaction between a metal ion and a ligand can be viewed as a Lewis acid–base reaction with the ligand donating a lone pair of electrons to an *empty* orbital of the metal ion to form a coordinate covalent bond:

**FIGURE 21.18**

A set of six d^2sp^3 hybrid orbitals on Co^{3+} can accept an electron pair from each of six NH_3 ligands to form the $\text{Co}(\text{NH}_3)_6^{3+}$ ion.



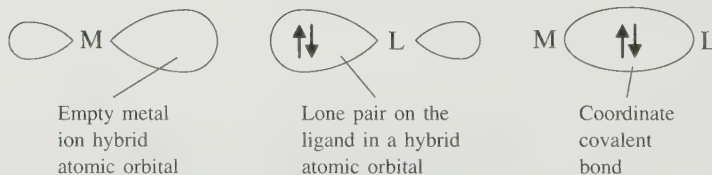
Tetrahedral ligand arrangement; sp^3 hybridization



Square planar ligand arrangement; dsp^2 hybridization



Linear ligand arrangement; sp hybridization



The hybrid orbitals used by the metal ion depend on the number and arrangement of the ligands. For example, accommodating the lone pairs from the six ammonia molecules in the octahedral $\text{Co}(\text{NH}_3)_6^{3+}$ ion requires a set of six empty hybrid atomic orbitals in an octahedral arrangement. As we discussed in Section 9.1, an octahedral set of orbitals is formed by the hybridization of two d , one s , and three p orbitals to give a set of six d^2sp^3 orbitals (see Fig. 21.18).

The hybrid orbitals required on a metal ion in a four-coordinate complex depend on whether the structure is tetrahedral or square planar. For a tetrahedral arrangement of ligands, an sp^3 hybrid set is required (see Fig. 21.19). For example, in the tetrahedral CoCl_4^{2-} ion, the Co^{2+} can be described as sp^3 hybridized. A square planar arrangement of ligands requires a dsp^2 hybrid orbital set on the metal ion (see Fig. 21.19). For example, in the square planar $\text{Ni}(\text{CN})_4^{2-}$ ion, the Ni^{2+} is described as dsp^2 hybridized.

A linear complex requires two hybrid orbitals 180 degrees from each other. This arrangement is given by an sp hybrid set (see Fig. 21.19). Thus, in the linear $\text{Ag}(\text{NH}_3)_2^+$ ion, the Ag^+ can be described as sp hybridized.

FIGURE 21.19

The hybrid orbitals required for tetrahedral, square planar, and linear complex ions. The metal ion hybrid orbitals are empty, and the metal ion bonds to the ligands by accepting lone pairs.

Although the localized electron model can account in a general way for metal–ligand bonds, it is rarely used today because it cannot readily account for important properties of complex ions, such as magnetism and color. Thus we will not pursue the model any further.

21.6 The Crystal Field Model

The main reason the localized electron model cannot fully account for the properties of complex ions is that it gives no information about how the energies of the d orbitals are affected by complex ion formation. This is critical because, as we will see, the color and magnetism of complex ions result from changes in the energies of the metal ion d orbitals caused by the metal–ligand interactions.

The **crystal field model** focuses on the energies of the d orbitals. In fact, this model is not so much a bonding model as it is an attempt to account for the colors and magnetic properties of complex ions. In its simplest form, the crystal field model assumes that the ligands can be approximated by *negative point charges* and that metal–ligand bonding is *entirely ionic*.

Octahedral Complexes

We will illustrate the fundamental principles of the crystal field model by applying it to an octahedral complex. Figure 21.20 shows the orientation of the $3d$ orbitals relative to an octahedral arrangement of point-charge ligands. The important thing to note is that two of the orbitals, d_{z^2} and $d_{x^2-y^2}$, point their lobes *directly* at the point-charge ligands and three of the orbitals, d_{xz} , d_{yz} , and d_{xy} , point their lobes *between* the point charges.

To understand the effect of this difference, we need to consider which type of orbital is lower in energy. Because the negative point-charge ligands repel negatively

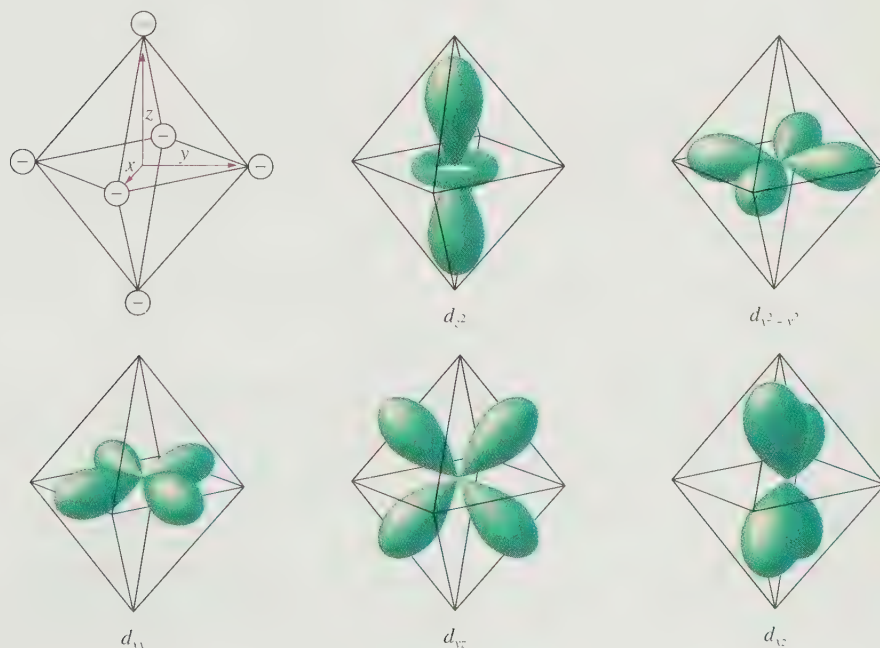
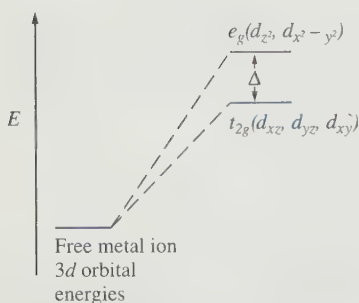
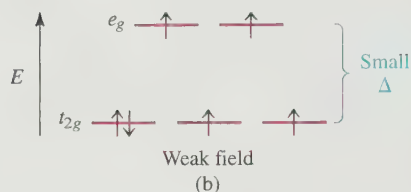
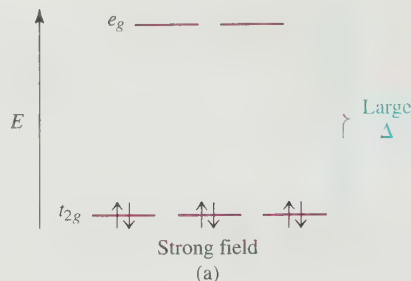


FIGURE 21.20

An octahedral arrangement of point-charge ligands and the orientation of the $3d$ orbitals.

**FIGURE 21.21**

The energies of the 3d orbitals for a metal ion in an octahedral complex. The 3d orbitals are degenerate (all have the same energy) in the free metal ion. In the octahedral complex the orbitals are split into two sets as shown. The difference in energy between the two sets is designated as Δ (delta).

**FIGURE 21.22**

Possible electron arrangements in the split 3d orbitals in an octahedral complex of Co^{3+} (electron configuration $3d^6$). (a) In a strong field (large Δ value), the electrons fill the t_{2g} set first, giving a diamagnetic complex. (b) In a weak field (small Δ value), the electrons occupy all five orbitals before any pairing occurs.

charged electrons, the electrons will first fill the d orbitals farthest from the ligands to minimize repulsions. In other words, the d_{xz} , d_{yz} , and d_{xy} orbitals (known as the t_{2g} set) are at a *lower energy* in the octahedral complex than are the d_{z^2} and $d_{x^2 - y^2}$ orbitals (the e_g set). This is shown in Fig. 21.21. The negative point-charge ligands increase the energies of all the d orbitals. However, the orbitals that point at the ligands are raised in energy more than those that point between the ligands.

It is this **splitting of the 3d orbital energies** (symbolized by Δ) that explains the color and magnetism of complex ions of the first-row transition metal ions. For example, in an octahedral complex of Co^{3+} (a metal ion with six 3d electrons), there are two possible ways to place the electrons in the split 3d orbitals (Fig. 21.22). If the splitting produced by the ligands is very large, a situation called the **strong-field case**, the electrons will pair in the lower-energy t_{2g} orbitals. This gives a *diamagnetic* complex in which all the electrons are paired. On the other hand, if the splitting is small (the **weak-field case**), the electrons will occupy all five orbitals before pairing occurs. In this case the complex has four unpaired electrons and is *paramagnetic*.

The crystal field model allows us to account for the differences in the magnetic properties of $\text{Co}(\text{NH}_3)_6^{3+}$ and CoF_6^{3-} . The $\text{Co}(\text{NH}_3)_6^{3+}$ ion is known to be diamagnetic and thus corresponds to the strong-field case, also called the **low-spin case**, since it yields the *minimum* number of unpaired electrons. In contrast, the CoF_6^{3-} ion, which is known to have four unpaired electrons, corresponds to the weak-field case, also known as the **high-spin case**, since it gives the *maximum* number of unpaired electrons.

SAMPLE EXERCISE 21.4

Crystal Field Model I

The $\text{Fe}(\text{CN})_6^{3-}$ ion is known to have one unpaired electron. Does the CN^- ligand produce a strong or weak field?

SOLUTION

Since the ligand is CN^- and the overall complex ion charge is $3-$, the metal ion must be Fe^{3+} , which has a $3d^5$ electron configuration. The two possible arrange-

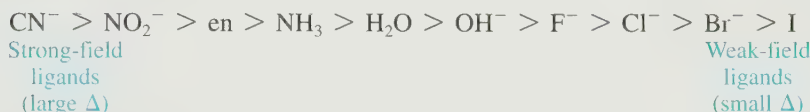
ments of the five electrons in the d orbitals split by the octahedrally arranged ligands are



The strong-field case gives one unpaired electron, which agrees with the experimental observation. The CN^- ion is a strong-field ligand toward the Fe^{3+} ion.

See Exercises 21.45 and 21.46.

From studies of many octahedral complexes, we can arrange ligands in order of their ability to produce d -orbital splitting. A partial listing of ligands in this **spectrochemical series** is



The ligands are arranged in order of decreasing Δ values toward a given metal ion.

It also has been observed that *the magnitude of Δ for a given ligand increases as the charge on the metal ion increases*. For example, NH_3 is a weak-field ligand toward Co^{2+} but acts as a strong-field ligand toward Co^{3+} . This makes sense; as the metal ion charge increases, the ligands will be drawn closer to the metal ion because of the increased charge density. As the ligands move closer, they cause greater splitting of the d orbitals and produce a larger Δ value.

SAMPLE EXERCISE 21.5

Crystal Field Model II

Predict the number of unpaired electrons in the complex ion $[\text{Cr}(\text{CN})_6]^{4-}$.

SOLUTION

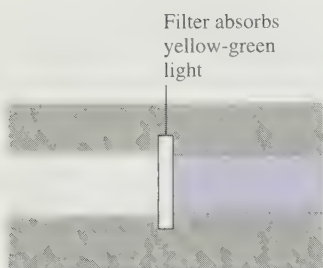
The net charge of $4-$ means that the metal ion present must be Cr^{2+} ($-6 + 2 = -4$), which has a $3d^4$ electron configuration. Since CN^- is a strong-field ligand (see the spectrochemical series), the correct crystal field diagram for $[\text{Cr}(\text{CN})_6]^{4-}$ is



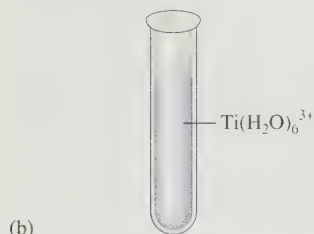
The complex ion will have two unpaired electrons. Note that the CN^- ligand produces such a large splitting that all four electrons will occupy the t_{2g} set even though two of the electrons must be paired in the same orbital.

See Exercises 21.47 and 21.48.

We have seen how the crystal field model can account for the magnetic properties of octahedral complexes. The same model also can explain the colors of these



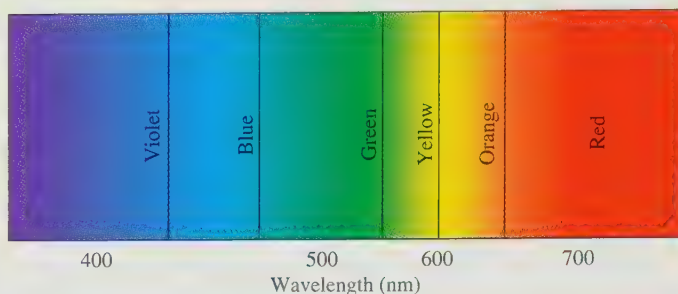
(a)



(b)

FIGURE 21.24

(a) When white light shines on a filter that absorbs in the yellow-green region, the emerging light is violet.
 (b) Because the complex ion $\text{Ti}(\text{H}_2\text{O})_6^{3+}$ absorbs yellow-green light, a solution of it is violet.

**FIGURE 21.23**

The visible spectrum.

complex ions. For example, $\text{Ti}(\text{H}_2\text{O})_6^{3+}$, an octahedral complex of Ti^{3+} , which has a $3d^1$ electron configuration, is violet because it absorbs light in the middle of the visible region of the spectrum (see Fig. 21.23). When a substance absorbs certain wavelengths of light in the visible region, the color of the substance is determined by the wavelengths of visible light that remain. We say that the substance exhibits the color *complementary* to those absorbed. The $\text{Ti}(\text{H}_2\text{O})_6^{3+}$ ion is violet because it absorbs light in the yellow-green region, thus letting red light and blue light pass, which gives the observed violet color. This is shown schematically in Fig. 21.24. Table 21.16 shows the general relationship between the wavelengths of visible light absorbed and the approximate color observed.

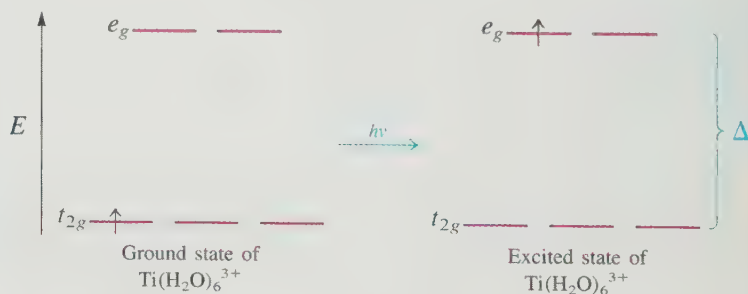
The reason that the $\text{Ti}(\text{H}_2\text{O})_6^{3+}$ ion absorbs a specific wavelength of visible light can be traced to the transfer of the lone d electron between the split d orbitals, as shown in Fig. 21.25. A given photon of light can be absorbed by a molecule only if the wavelength of the light provides exactly the energy needed by the molecule. Or, in other words, the wavelength absorbed is determined by the relationship

$$\Delta E = \frac{hc}{\lambda}$$

where ΔE represents the energy spacing in the molecule (we have used simply Δ in this chapter) and λ represents the wavelength of light needed. Because the d -orbital splitting in most octahedral complexes corresponds to the energies of photons in the visible region, octahedral complex ions are usually colored.

TABLE 21.16 Approximate Relationship of Wavelength of Visible Light Absorbed to Color Observed

Absorbed Wavelength in nm (Color)	Observed Color
400 (violet)	Greenish yellow
450 (blue)	Yellow
490 (blue-green)	Red
570 (yellow-green)	Violet
580 (yellow)	Dark blue
600 (orange)	Blue
650 (red)	Green

**FIGURE 21.25**

The complex ion $\text{Ti}(\text{H}_2\text{O})_6^{3+}$ can absorb visible light in the yellow-green region to transfer the lone d electron from the t_{2g} to the e_g set.



TABLE 21.17
Several Octahedral
Complexes of Cr^{3+} and Their
Colors

Isomer	Color
$[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$	Violet
$[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2$	Blue-green
$[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}$	Green
$[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$	Yellow
$[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$	Purple
$[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$	Violet

Since the ligands coordinated to a given metal ion determine the size of the d -orbital splitting, the color changes as the ligands are changed. This occurs because a change in Δ means a change in the wavelength of light needed to transfer electrons between the t_{2g} and e_g orbitals. Several octahedral complexes of Cr^{3+} and their colors are listed in Table 21.17.

Other Coordination Geometries

Using the same principles developed for octahedral complexes, we will now consider complexes with other geometries. For example, Fig. 21.26 shows a tetrahedral arrangement of point charges in relation to the $3d$ orbitals of a metal ion. There are two important facts to note:

1. None of the $3d$ orbitals “point at the ligands” in the tetrahedral arrangement, as the $d_{x^2-y^2}$ and d_{z^2} orbitals do in the octahedral case. Thus the tetrahedrally arranged ligands do not differentiate the d orbitals as much in the tetrahedral as in the octahedral case. That is, the difference in energy between the split d orbitals will be significantly less in tetrahedral complexes. Although we will not derive it here, the tetrahedral splitting is $\frac{4}{9}$ that of the octahedral splitting for a given ligand and metal ion:

$$\Delta_{\text{tet}} = \frac{4}{9}\Delta_{\text{oct}}$$

2. Although not exactly pointing at the ligands, the d_{xy} , d_{xz} , and d_{yz} orbitals are closer to the point charges than are the d_{z^2} and $d_{x^2-y^2}$ orbitals. This means that the tetrahedral d -orbital splitting will be opposite to that for the octahedral arrangement. The two arrangements are contrasted in Fig. 21.27. Because the d -orbital splitting is relatively small for the tetrahedral case, the weak-field case (high-spin case) *always* applies. There are no known ligands powerful enough to produce the strong-field case in a tetrahedral complex.



Solutions of $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$ (yellow) and $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ (purple).

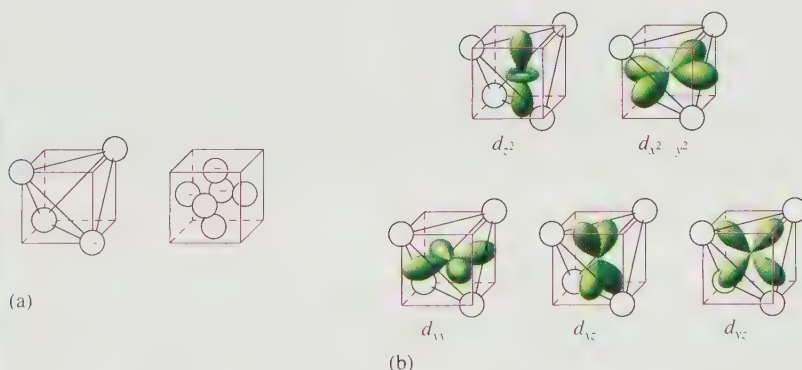


FIGURE 21.26

(a) Tetrahedral and octahedral arrangements of ligands shown inscribed in cubes. Note that in the two types of arrangements, the point charges occupy opposite parts of the cube; the octahedral point charges are at the centers of the cube faces, and the tetrahedral point charges occupy opposite corners of the cube. (b) The orientations of the $3d$ orbitals relative to the tetrahedral set of point charges.

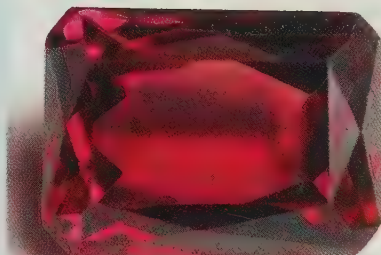
CHEMICAL IMPACT

Transition Metal Ions Lend Color to Gems

The beautiful pure color of gems, so valued by cultures everywhere, arises from trace transition metal ion impurities in minerals that would otherwise be colorless. For example, the stunning red of a ruby, the most valuable of all gemstones, is caused by Cr^{3+} ions, which replace about 1% of the Al^{3+} ions in the mineral corundum, which is a form of aluminum oxide (Al_2O_3) that is nearly as hard as diamond. In the corundum structure the Cr^{3+} ions are surrounded by six oxide ions at the vertices of an octahedron. This leads to the characteristic octahedral splitting of chromium's 3d orbitals, such that the Cr^{3+} ions absorb strongly in the blue-violet and yellow-green regions of the visible spectrum but transmit red light to give the characteristic ruby color. (On the other hand, if some of the Al^{3+} ions in corundum are replaced by a mixture of Fe^{2+} , Fe^{3+} , and Ti^{4+} ions, the gem is a sapphire with its brilliant blue color; or if some of the Al^{3+} ions are replaced by Fe^{3+} ions, the stone is a yellow topaz.)

Emeralds are derived from the mineral beryl, a beryllium aluminum silicate (empirical formula $3\text{BeO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$). When some of the Al^{3+} ions in beryl are replaced by Cr^{3+} ions, the characteristic green color of emerald results. In this environment the splitting of the Cr^{3+} 3d orbitals causes it to strongly absorb yellow and blue-violet light and to transmit green light.

A gem closely related to ruby and emerald is alexandrite, named after Alexander II of Russia. This gem is based on the mineral chrysoberyl, a beryllium aluminate with the empirical formula $\text{BeO} \cdot \text{Al}_2\text{O}_3$ in which approximately 1% of the Al^{3+} ions are replaced by Cr^{3+} ions. In the chrysoberyl environment Cr^{3+} absorbs strongly in the yellow region of the spectrum. Alexandrite has the interesting property of changing colors depending on the light source. When the first alexandrite stone was discovered deep in a mine in the Rus-



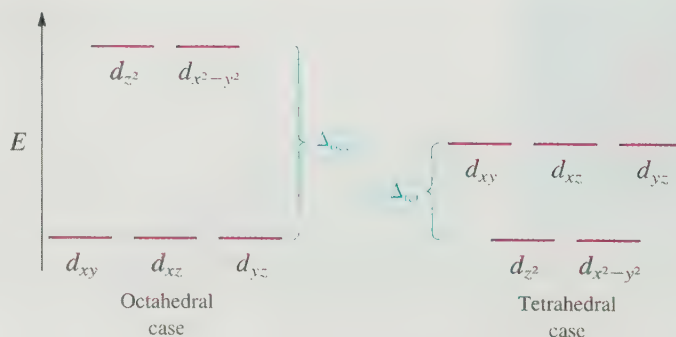
Alexandrite, a gem closely related to ruby and emerald.

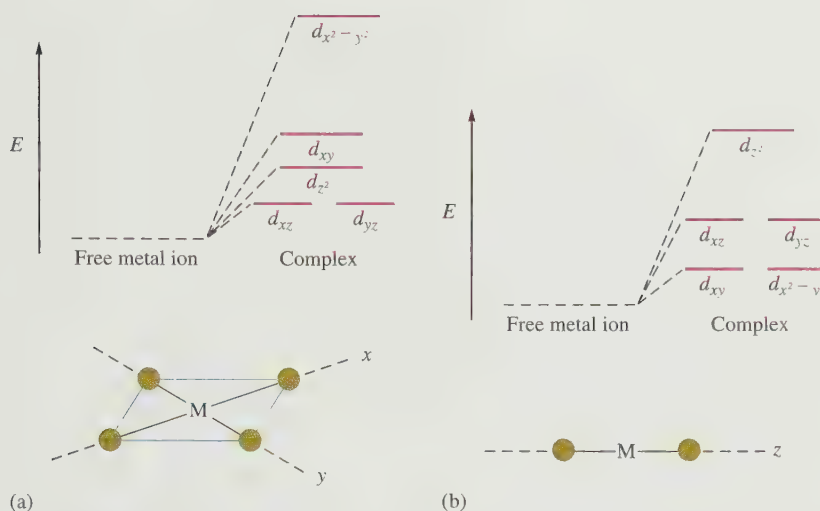
sian Ural Mountains in 1831, it appeared to be a deep red color in the firelight of the miners' lamps. However, when the stone was brought to the surface, its color was blue. This seemingly magical color change occurs because the firelight of a miner's helmet is rich in the yellow and red wavelengths of the visible spectrum but does not contain much blue. Absorption of the yellow by the stone produces a reddish color. However, daylight has much more intensity in the blue region than firelight. Thus the extra blue in the light transmitted by the stone gives it bluish color in daylight.

Once the structure of a natural gem is known, it is usually not very difficult to make the gem artificially. For example, rubies and sapphires are made on a large scale by fusing $\text{Al}(\text{OH})_3$ with the appropriate transition metal salts at approximately 1200°C to make the "doped" corundum. With these techniques gems of astonishing size can be manufactured: Rubies as large as 10 lb and sapphires up to 100 lb have been synthesized. Smaller synthetic stones produced for jewelry are virtually identical to the corresponding natural stones, and it takes great skill for a gemologist to tell the difference.

FIGURE 21.27

The crystal field diagrams for octahedral and tetrahedral complexes. The relative energies of the sets of d orbitals are reversed. For a given type of ligand, the splitting is much larger for the octahedral complex ($\Delta_{\text{oct}} > \Delta_{\text{tet}}$) because in this arrangement the d_{z^2} and $d_{x^2-y^2}$ point their lobes directly at the point charges and are thus relatively high in energy.



**FIGURE 21.28**

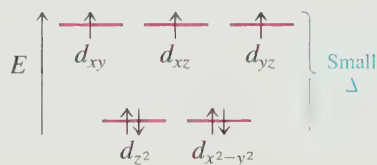
(a) The crystal field diagram for a square planar complex oriented in the xy plane with ligands along the x and y axes. The position of the d_{z^2} orbital is higher than those of the d_{xz} and d_{yz} orbitals because of the “doughnut” of electron density in the xy plane. The actual position of d_{z^2} is somewhat uncertain and varies in different square planar complexes. (b) The crystal field diagram for a linear complex where the ligands lie along the z axis.

SAMPLE EXERCISE 21.6**Crystal Field Model III**

Give the crystal field diagram for the tetrahedral complex ion CoCl_4^{2-} .

SOLUTION

The complex ion contains Co^{2+} , which has a $3d^7$ electron configuration. The splitting of the d orbitals will be small, since this is a tetrahedral complex, giving the high-spin case with three unpaired electrons.



See Exercises 21.51 through 21.54.

The crystal field model also applies to square planar and linear complexes. The crystal field diagrams for these cases are shown in Fig. 21.28. The ranking of orbitals in these diagrams can be explained by considering the relative orientations of the point charges and the orbitals. The diagram in Fig. 21.27 for the octahedral arrangement can be used to obtain these orientations. We can obtain the square planar complex by removing the two point charges along the z axis. This will greatly lower the energy of d_{z^2} , leaving only $d_{x^2-y^2}$, which points at the four remaining ligands as the highest-energy orbital. We can obtain the linear complex from the octahedral arrangement by leaving the two ligands along the z axis and removing the four in the xy plane. This means that only the d_{z^2} points at the ligands and is highest in energy.

TABLE 21.18 The First-Row Transition Metals and Their Biologic Significance

First-Row Transition Metal	Biologic Function(s)
Scandium	None known.
Titanium	None known.
Vanadium	None known in humans.
Chromium	Assists insulin in the control of blood sugar; may also be involved in the control of cholesterol.
Manganese	Necessary for a number of enzymatic reactions.
Iron	Component of hemoglobin and myoglobin; involved in the electron-transport chain.
Cobalt	Component of vitamin B ₁₂ , which is essential for the metabolism of carbohydrates, fats, and proteins.
Nickel	Component of the enzymes urease and hydrogenase.
Copper	Component of several enzymes; assists in iron storage; involved in the production of color pigments of hair, skin, and eyes.
Zinc	Component of insulin and many enzymes.

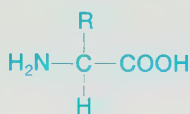
21.7 The Biologic Importance of Coordination Complexes

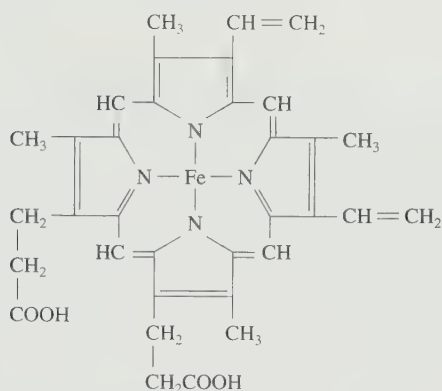
The ability of metal ions to coordinate with and release ligands and to easily undergo oxidation and reduction makes them ideal for use in biologic systems. For example, metal ion complexes are used in humans for the transport and storage of oxygen, as electron-transfer agents, as catalysts, and as drugs. Most of the first-row transition metals are essential for human health, as summarized in Table 21.18. We will concentrate on iron's role in biologic systems, since several of its coordination complexes have been studied extensively.

Iron plays a central role in almost all living cells. In mammals, the principal source of energy comes from the oxidation of carbohydrates, proteins, and fats. Although oxygen is the oxidizing agent for these processes, it does not react directly with these molecules. Instead, the electrons from the breakdown of these nutrients are passed along a complex chain of molecules, called the *respiratory chain*, eventually reaching the O₂ molecule. The principal electron-transfer molecules in the respiratory chain are iron-containing species called **cytochromes**, consisting of two main parts: an iron complex called **heme** and a protein. The structure of the heme complex is shown in Fig. 21.29. Note that it contains an iron ion (it can be either Fe²⁺ or Fe³⁺) coordinated to a rather complicated planar ligand called a **porphyrin**. As a class, porphyrins all contain the same central ring structure but have different substituent groups at the edges of the rings. The various porphyrin molecules act as tetradentate ligands for many metal ions, including iron, cobalt, and magnesium. In fact, *chlorophyll*, a substance essential to the process of photosynthesis, is a magnesium–porphyrin complex of the type shown in Fig. 21.30.

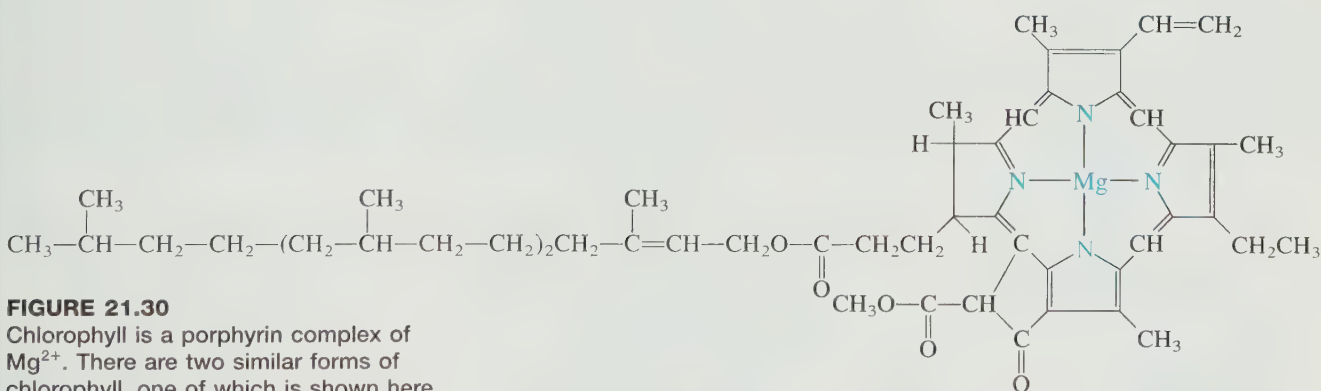
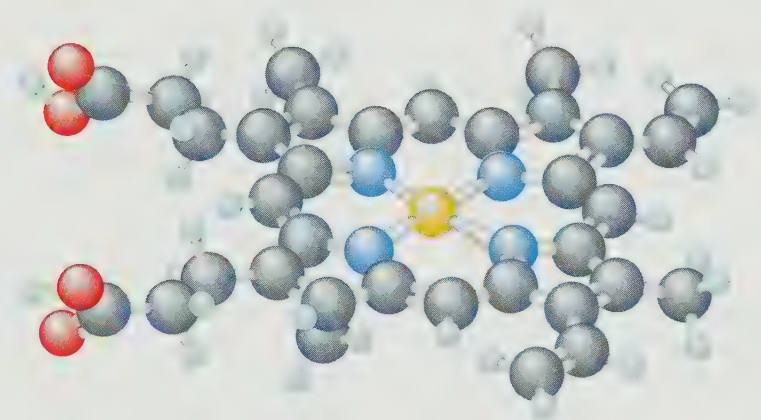
In addition to participating in the transfer of electrons from nutrients to oxygen, iron plays a principal role in the transport and storage of oxygen in mammalian blood and tissues. Oxygen is stored in a molecule called **myoglobin**, which consists of a heme complex and a protein in a structure very similar to that of the cytochromes. In myoglobin, the Fe²⁺ ion is coordinated to four nitrogen atoms of the porphyrin ring and to a nitrogen atom of the protein chain, as shown in Fig. 21.31. Since Fe²⁺

A protein is a large molecule assembled from amino acids, which have the general structure in which R represents various groups.



**FIGURE 21.29**

The heme complex, in which an Fe^{2+} ion is coordinated to four nitrogen atoms of a planar porphyrin ligand.

**FIGURE 21.30**

Chlorophyll is a porphyrin complex of Mg^{2+} . There are two similar forms of chlorophyll, one of which is shown here.

is normally six-coordinate, this leaves one position open for attachment of an O_2 molecule.

One especially interesting feature of myoglobin is that it involves an O_2 molecule attaching directly to Fe^{2+} . However, if gaseous O_2 is bubbled into an aqueous solution containing heme, the Fe^{2+} is immediately oxidized to Fe^{3+} . This oxidation of the Fe^{2+} in heme does not happen in myoglobin. This fact is of crucial importance because Fe^{3+} does not form a coordinate covalent bond with O_2 , and myoglobin would not function if the bound Fe^{2+} could be oxidized. Since the Fe^{2+} in the “bare” heme complex can

CHEMICAL IMPACT

The Danger of Mercury*

In August 1989, four family members from Lincoln Park, Michigan, died under mysterious circumstances. All four victims had severe tissue damage to the esophagus and lungs, which led doctors to suspect exposure to some type of caustic chemical. Subsequently, local police and fire investigators discovered a crude laboratory in the basement that was used to recover valuable silver from stolen dental amalgams. A dental amalgam is a metal alloy that a dentist uses to fill a tooth. The alloy typically contains silver, tin, copper, and zinc dissolved in liquid mercury. The mixture is placed in a cavity, where it hardens, resulting in a standard “filling.”

One of the victims worked at a manufacturing facility for amalgams and was stealing some of the products. At home in his crude lab he heated the amalgam to drive off the mercury (which vaporized at relatively low temperatures) so that he could recover the silver that was left behind. In the process, the colorless, odorless, tasteless mercury vapor entered the ductwork of the home, which was contaminated with mercury at levels 1500 times normal—levels certain to result in death to those exposed. In fact, postmortem analysis revealed extreme levels of mercury in the vital organs of all four victims. Mercury vapor was the silent killer.

The toxicity of mercury varies significantly depending on the route of entry into the body. Inhalation is the most dangerous route because mercury vapor entering the lungs quickly passes across the lung–blood barrier and into the bloodstream, where it can interfere with normal blood chemistry. One of the reactions that takes place in the blood is

the decomposition of hydrogen peroxide (a metabolic waste product) by the enzyme peroxidase:



When elemental mercury enters the bloodstream, it reacts with hydrogen peroxide in the presence of peroxidase to produce mercury(II) oxide and water:

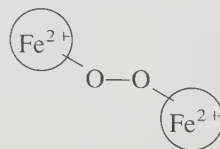


If this conversion to mercury(II) occurs within vital tissues, the mercury(II) cation can denature proteins, inhibit enzyme activity, and disrupt cell membranes. Death often results from respiratory or kidney failure.

If mercury is so toxic, how can it be used in dental fillings? Surprisingly, unlike elemental mercury in the vapor form, mercury bound as a solid in a dental amalgam presents little, if any, risk. Because the mercury is not mobile, even in the harsh environment of the human mouth, the American Dental Association has determined it to be a minimal health risk to dental patients. Even if a filling loosens and is accidentally swallowed, it is passed through the digestive system and excreted before it can pose any risk. The mercury that the four victims in this story were exposed to resulted from heating the amalgam in a smelting furnace, thus vaporizing the mercury and exposing the occupants of the house to the most hazardous route of entry—inhalation.

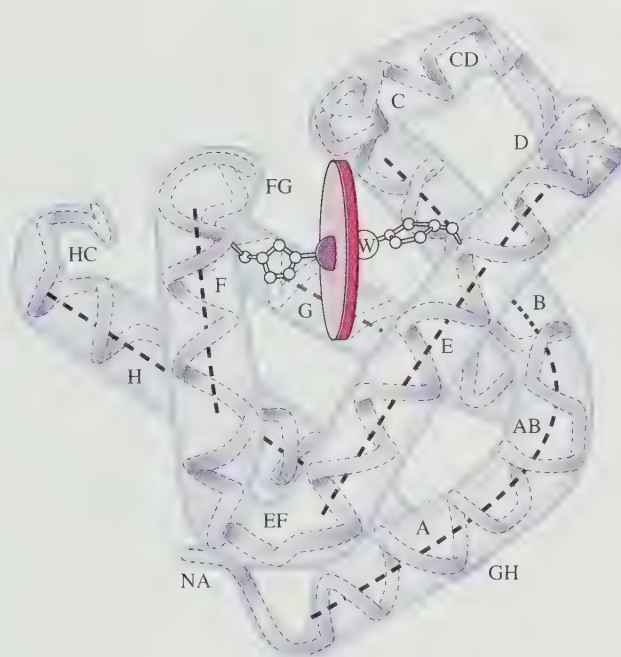
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be oxidized, it must be the protein that somehow prevents the oxidation. How? Based on much research, the answer seems to be that the oxidation of Fe^{2+} to Fe^{3+} involves an oxygen bridge between two iron ions (the circles indicate the ligands):

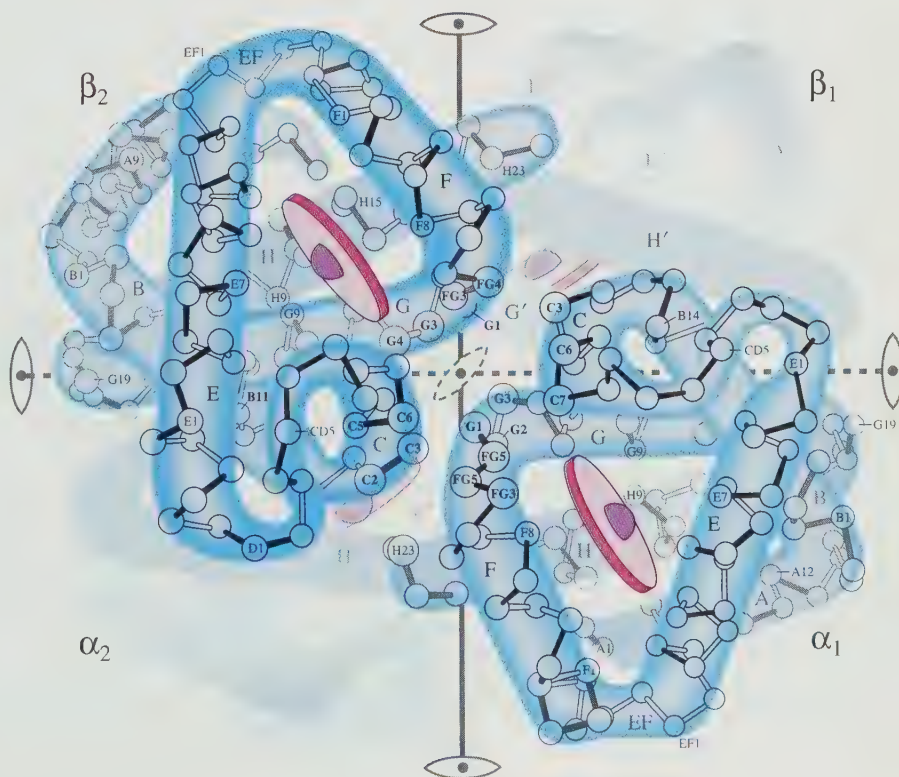


The bulky protein around the heme group in myoglobin prevents two molecules from getting close enough to form the oxygen bridge, and so oxidation of the Fe^{2+} is prevented.

The transport of O_2 in the blood is carried out by **hemoglobin**, a molecule consisting of four myoglobin-like units, as shown in Fig. 21.32. Each hemoglobin can therefore bind four O_2 molecules to form a bright red diamagnetic complex. The

**FIGURE 21.31**

A representation of the myoglobin molecule. The Fe^{2+} ion is coordinated to four nitrogen atoms in the porphyrin of the heme (represented by the disk in the figure) and on nitrogen from the protein chain. This leaves a sixth coordination position (indicated by the W) available for an oxygen molecule.

**FIGURE 21.32**

A representation of the hemoglobin structure. There are two slightly different types of protein chains (α and β). Each hemoglobin has two α chains and two β chains, each with a heme complex near the center. Thus each hemoglobin molecule can complex with four O_2 molecules.

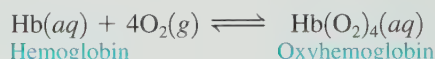
**FIGURE 21.33**

A normal red blood cell (right) and a sickle cell (left), both magnified 18,000 times.

diamagnetism occurs because oxygen is a strong-field ligand toward Fe^{2+} , which has a $3d^6$ electron configuration. When the oxygen molecule is released, water molecules occupy the sixth coordination position around each Fe^{2+} , giving a bluish paramagnetic complex (H_2O is a weak-field ligand toward Fe^{2+}) that gives venous blood its characteristic bluish tint.

Hemoglobin dramatically demonstrates how sensitive the function of a biomolecule is to its structure. In certain people, in the synthesis of the proteins needed for hemoglobin, an improper amino acid is inserted into the protein in two places. This may not seem very serious, since there are several hundred amino acids present. However, because the incorrect amino acid has a nonpolar substituent instead of the polar one found on the proper amino acid, the hemoglobin drastically changes its shape. The red blood cells are then sickle-shaped rather than disk-shaped, as shown in Fig. 21.33. The misshapen cells can aggregate, causing clogging of tiny capillaries. This condition, known as *sickle cell anemia*, is the subject of intense research.

Our knowledge of the workings of hemoglobin allows us to understand the effects of high altitudes on humans. The reaction between hemoglobin and oxygen can be represented by the following equilibrium:



At high altitudes, where the oxygen content of the air is lower, the position of this equilibrium will shift to the left, according to Le Châtelier's principle. Because less oxyhemoglobin is formed, fatigue, dizziness, and even a serious illness called *high-altitude sickness* can result. One way to combat this problem is to use supplemental oxygen, as most high-altitude mountain climbers do. However, this is impractical for people who live at high elevations. In fact, the human body adapts to the lower oxygen concentrations by making more hemoglobin, causing the equilibrium to shift back to the right. Someone moving from Chicago to Boulder, Colorado (5300 feet), would notice the effects of the new altitude for a couple of weeks, but as the hemoglobin level increased, the effects would disappear. This change is called *high-altitude acclimatization*, which explains why athletes who want to compete at high elevations should practice there for several weeks prior to the event.

Our understanding of the biologic role of iron also allows us to explain the toxicities of substances such as carbon monoxide and the cyanide ion. Both CO and



Sherpa and Balti porters are acclimatized to high elevations such as those around the K2 mountain peak in Pakistan.

CHEMICAL IMPACT

Supercharged Blood

During the 1964 Winter Olympics in Innsbruck, Austria, a Finn named Eero Maentyranta won three gold medals in cross-country skiing and immediately became a national hero. His success was due in no small part to the fact that his blood carried 25% to 50% more hemoglobin than the average man's blood. Maentyranta suffered from a rare genetic disorder that results in unusually elevated levels of red blood cells. This extra oxygen-carrying capacity lends itself to increased stamina and endurance, certainly an advantage in the rigorous sport of cross-country skiing. Several years later, geneticists at the University of Helsinki determined that the disorder was due to a mutation of a protein responsible for red blood cell production called the *erythropoietin receptor* (EPO-R). The mutation, which was common in the Maentyranta family, resulted in a protein that was missing 70 amino acids (out of 550). This mutation deleted the portion of the protein that contained the "off switch" for red blood cell production.

Since the discovery of EPO's role in red blood cell production, genetic engineers have been able to synthesize EPO by bioengineering techniques. The protein, marketed in the United States by Amgen of Thousand Oaks, California, is used by kidney dialysis, AIDS, and cancer patients to boost red blood cell production. It has become biotechnology's biggest revenue producer, with over \$1 billion in annual sales.

While the potential benefits of this protein are obvious, the potential for abuse may be even greater. The Tour de France, thought by many to be the world's greatest endurance race, was rocked in 1998 by controversy when several riders (including three race favorites) were expelled from the race over allegations of blood doping with the red blood cell-enhancing hormone EPO. EPO has become the drug of choice for many endurance athletes trying to gain an unfair advantage because it is metabolized quickly and, being identical to the body's own EPO, is almost impossi-



The 1998 Tour de France.

ble to detect by blood or urine analysis. But the hazards are great. Endurance athletes are especially at risk from abuse of EPO due to extreme water loss during the athletic competition, which, when coupled with elevated levels of EPO, results in an extreme thickening of the blood. This puts an obvious strain on the heart. Since EPO became available in 1986, several world-class athletes (mostly bicyclists and distance runners) have died under mysterious circumstances thought to be associated with abuse of EPO. Because of the widespread abuse of EPO, new methods of detection are being put in place to limit its impact on organized sports and its participants.

The advantage that Eero Maentyranta gained in the 1964 Olympics was the result of a disorder that he had lived with for his entire life. His body had become accustomed to operating with elevated levels of hemoglobin, and it became a natural advantage. Synthetic EPO holds much promise for those suffering conditions that result in hemoglobin deficiency. But as a performance-enhancing drug, EPO's advantages come with enormous risk.

CN^- are very good ligands toward iron and so can interfere with the normal workings of the iron complexes in the body. For example, carbon monoxide has about 200 times the affinity for the Fe^{2+} in hemoglobin as oxygen does. The resulting stable complex, **carboxyhemoglobin**, prevents the normal uptake of O_2 , thus depriving the body of needed oxygen. Asphyxiation can result if enough carbon monoxide is present in the air. The mechanism for the toxicity of the cyanide ion is somewhat different. Cyanide coordinates strongly to cytochrome oxidase, an iron-containing cytochrome enzyme that catalyzes the oxidation–reduction reactions of certain cytochromes. The coordinated cyanide thus prevents the electron-transfer process and rapid death results. Because of its behavior, cyanide is called a *respiratory inhibitor*.

21.8 Metallurgy and Iron and Steel Production

In the preceding section we saw the importance of iron in biologic systems. Of course, iron is also very important in many other ways in our world. In this section we will discuss the isolation of metals from their natural sources and the formulation of metals into useful materials, with special emphasis on the role of iron.

Metals are very important for structural applications, electrical wires, cooking utensils, tools, decorative items, and many other purposes. However, because the main chemical characteristic of a metal is its ability to give up electrons, almost all metals in nature are found in ores, combined with nonmetals such as oxygen, sulfur, and the halogens. To recover and use these metals, we must separate them from their ores and reduce the metal ions. Then, because most metals are unsuitable for use in the pure state, we must form alloys that have the desired properties. The process of separating a metal from its ore and preparing it for use is known as **metallurgy**. The steps in this process are typically

1. Mining
2. Pretreatment of the ore
3. Reduction to the free metal
4. Purification of the metal (refining)
5. Alloying

An ore can be viewed as a mixture containing **minerals** (relatively pure metal compounds) and **gangue** (sand, clay, and rock). Some typical minerals are listed in Table 21.19. Although silicate minerals are the most common in the earth's crust, they are typically very hard and difficult to process, making metal extraction relatively expensive. Therefore, other ores are used when available.

After mining, an ore must be treated to remove the gangue and to concentrate the mineral. The ore is first pulverized and then processed in a variety of devices, including cyclone separators (see Fig. 21.34), inclined vibrating tables, and flotation tanks.

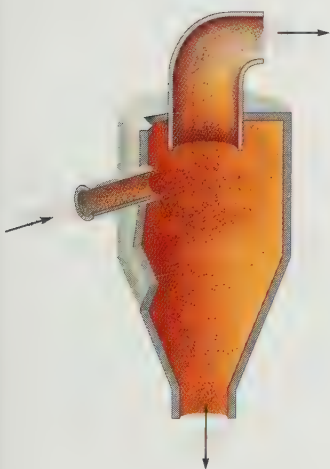
In the **flotation process**, the crushed ore is fed into a tank containing a water–oil–detergent mixture. Because of the difference in the surface characteristics of the mineral particles and the silicate rock particles, the oil wets the mineral particles. A stream of air blown through the mixture causes tiny bubbles to form on the oil-covered pieces, which then float to the surface, where they can be skimmed off.



A steel mill in Brazil.

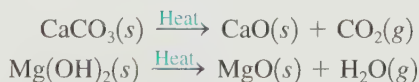
TABLE 21.19 Common Minerals Found in Ores

Anion	Examples
None (free metal)	Au, Ag, Pt, Pd, Rh, Ir, Ru
Oxide	Fe ₂ O ₃ (hematite) Fe ₃ O ₄ (magnetite) Al ₂ O ₃ (bauxite) SnO ₂ (cassiterite)
Sulfide	PbS (galena) ZnS (sphalerite) FeS ₂ (pyrite) HgS (cinnabar) Cu ₂ S (chalcocite)
Chloride	NaCl (rock salt) KCl (sylvite) KCl · MgCl ₂ (carnallite)
Carbonate	FeCO ₃ (siderite) CaCO ₃ (limestone) MgCO ₃ (magnesite) MgCO ₃ · CaCO ₃ (dolomite)
Sulfate	CaSO ₄ · 2H ₂ O (gypsum) BaSO ₄ (barite)
Silicate	Be ₃ Al ₂ Si ₆ O ₁₈ (beryl) Al ₂ (Si ₂ O ₈)(OH) ₄ (kaolinite) LiAl(SiO ₃) ₂ (spodumene)

**FIGURE 21.34**

A schematic diagram of a cyclone separator. The ore is pulverized and blown into the separator. The more dense mineral particles are thrown toward the walls by centrifugal force and fall down the funnel. The lighter particles (gangue) tend to stay closer to the center and are drawn out through the top by the stream of air.

After the mineral has been concentrated, it is often chemically altered in preparation for the reduction step. For example, nonoxide minerals are often converted to oxides before reduction. Carbonates and hydroxides can be converted by simple heating:



Sulfide minerals can be converted to oxides by heating in air at temperatures below their melting points, a process called **roasting**:



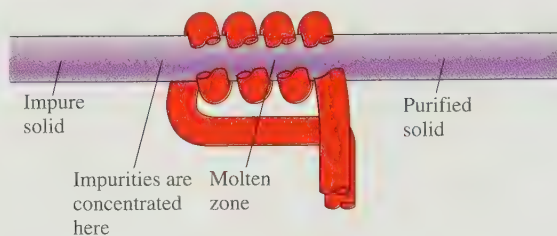
As we have seen earlier, sulfur dioxide causes severe problems if released into the atmosphere, and modern roasting operations collect this gas and use it in the manufacture of sulfuric acid.

The method chosen to reduce the metal ion to the free metal, a process called **smelting**, depends on the affinity of the metal ion for electrons. Some metals are good enough oxidizing agents that the free metal is produced in the roasting process. For example, the roasting reaction for cinnabar is



where the Hg^{2+} is reduced by electrons donated by the S^{2-} ion, which is then further oxidized by O_2 to form SO_2 .

The roasting of a more active metal produces the metal oxide, which must be reduced to obtain the free metal. The most common reducing agents are coke

**FIGURE 21.35**

A schematic representation of zone refining.

(impure carbon), carbon monoxide, and hydrogen. The following are some common examples of the reduction process:



The most active metals, such as aluminum and the alkali metals, must be reduced electrolytically, usually from molten salts (see Section 17.8).

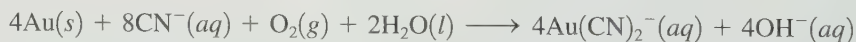
The metal obtained in the reduction step is invariably impure and must be refined. The methods of refining include electrolytic refining (see Section 17.8), oxidation of impurities (as for iron, see below), and distillation of low-boiling metals such as mercury and zinc. One process used when highly pure metals are needed is **zone refining**. In this process a bar of the impure metal travels through a heater (see Fig. 21.35), which causes melting and recrystallizing of the metal as the bar cools. Purification of the metal occurs because as the crystal re-forms, the metal ions are likely to fit much better in the crystal lattice than are the atoms of impurities. Thus the impurities tend to be excluded and carried to the end of the bar. Several repetitions of this process give a very pure metal bar.

Hydrometallurgy

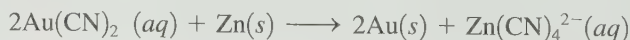
The metallurgical processes we have considered so far are usually called **pyrometallurgy** (*pyro* means “at high temperatures”). These traditional methods require large quantities of energy and have two other serious problems: atmospheric pollution (mainly by sulfur dioxide) and relatively high costs that make treatment of low-grade ores economically unfeasible.

In the past hundred years, a different process, **hydrometallurgy** (*hydro* means “water”), has been employed to extract metals from ores by use of aqueous chemical solutions, a process called **leaching**. The first two uses of hydrometallurgy were for the extraction of gold from low-grade ores and for the production of aluminum oxide, or alumina, from bauxite, an aluminum-bearing ore.

Gold is sometimes found in ores in the elemental state, but it usually occurs in relatively small concentrations. A process called **cyanidation** treats the crushed ore with an aqueous cyanide solution in the presence of air to dissolve the gold by forming the complex ion $\text{Au}(\text{CN})_2^-$:



Pure gold is then recovered by reaction of the solution of $\text{Au}(\text{CN})_2^-$ with zinc powder to reduce Au^+ to Au:



The extraction of alumina from bauxite (the Bayer process) leaches the ore with sodium hydroxide at high temperatures and pressures to dissolve the amphoteric aluminum oxide:



This process leaves behind solid impurities such as SiO_2 , Fe_2O_3 , and TiO_2 , which are not appreciably soluble in basic solution. After the solid impurities are removed, the pH of the solution is lowered, causing the pure aluminum oxide to re-form. It is then electrolyzed to produce aluminum metal (see Section 17.8).

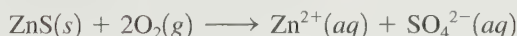
As illustrated by these processes, hydrometallurgy involves two distinct steps: *selective leaching* of a given metal ion from the ore and recovery of the metal ion from the solution by *selective precipitation* as an ionic compound.

The leaching agent can simply be water if the metal-containing compound is a water-soluble chloride or sulfate. However, most commonly, the metal is present in a water-insoluble substance that must somehow be dissolved. The leaching agents used in such cases are usually aqueous solutions containing acids, bases, oxidizing agents, salts, or some combination of these. Often the dissolving process involves the formation of complex ions. For example, when an ore containing water-insoluble lead sulfate is treated with an aqueous sodium chloride solution, the soluble complex ion PbCl_4^{2-} is formed:



Formation of a complex ion also occurs in the cyanidation process for the recovery of gold. However, since the gold is present in the ore as particles of metal, it must first be oxidized by oxygen to produce Au^+ , which then reacts with CN^- to form the soluble $\text{Au}(\text{CN})_2^-$ species. Thus, in this case, the leaching process involves a combination of oxidation and complexation.

Sometimes just oxidation is used. For example, insoluble zinc sulfide can be converted to soluble zinc sulfate by pulverizing the ore and suspending it in water to form a slurry through which oxygen is bubbled:



One advantage of hydrometallurgy over the traditional processes is that sometimes the leaching agent can be pumped directly into the ore deposits in the earth. For example, aqueous sodium carbonate (Na_2CO_3) can be injected into uranium-bearing ores to form water-soluble complex carbonate ions.

Recovering the metal ions from the leaching solution involves forming an insoluble solid containing the metal ion to be recovered. This step may involve addition of an anion to form an insoluble salt, reduction to the solid metal, or a combination of reduction and precipitation of a salt. Examples of these processes are shown in Table 21.20. Because of its suitability for treating low-grade ores economically and without significant pollution, hydrometallurgy is becoming more popular for recovering many important metals such as copper, nickel, zinc, and uranium.

The Metallurgy of Iron

Iron is present in the earth's crust in many types of minerals. *Iron pyrite* (FeS_2) is widely distributed but is not suitable for production of metallic iron and steel because it is almost impossible to remove the last traces of sulfur. The presence of sulfur makes the resulting steel too brittle to be useful. *Siderite* (FeCO_3) is a valuable iron mineral that can be converted to iron oxide by heating. The iron oxide

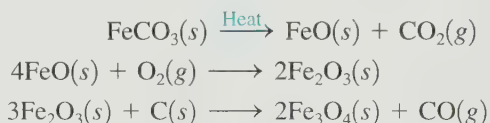
Precipitation reactions are discussed in Section 15.7.

TABLE 21.20 Examples of Methods for Recovery of Metal Ions from Leaching Solutions

Method	Examples
Precipitation of a salt	$\text{Cu}^{2+}(\text{aq}) + \text{S}^{2-}(\text{aq}) \longrightarrow \text{CuS}(\text{s})$ $\text{Cu}^{+}(\text{aq}) + \text{HCN}(\text{aq}) \longrightarrow \text{CuCN}(\text{s}) + \text{H}^{+}(\text{aq})$
Reduction	$\left\{ \begin{array}{l} \text{Chemical} \\ \text{Electrolytic} \end{array} \right.$ $\left\{ \begin{array}{l} \text{Au}^{+}(\text{aq}) + \text{Fe}^{2+}(\text{aq}) \longrightarrow \text{Au}(\text{s}) + \text{Fe}^{3+}(\text{aq}) \\ \text{Cu}^{2+}(\text{aq}) + \text{Fe}(\text{s}) \longrightarrow \text{Cu}(\text{s}) + \text{Fe}^{2+}(\text{aq}) \\ \text{Ni}^{2+}(\text{aq}) + \text{H}_2(\text{g}) \longrightarrow \text{Ni}(\text{s}) + 2\text{H}^{+}(\text{aq}) \\ \text{Cu}^{2+}(\text{aq}) + 2\text{e}^{-} \longrightarrow \text{Cu}(\text{s}) \\ \text{Al}^{3+}(\text{aq}) + 3\text{e}^{-} \longrightarrow \text{Al}(\text{s}) \end{array} \right.$
Reduction plus precipitation	$2\text{Cu}^{2+}(\text{aq}) + 2\text{Cl}^{-}(\text{aq}) + \text{H}_2\text{SO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \longrightarrow 2\text{CuCl}(\text{s}) + 3\text{H}^{+}(\text{aq}) + \text{HSO}_4^{-}(\text{aq})$

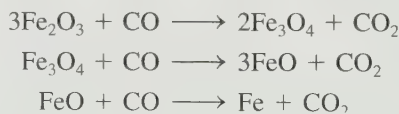
minerals are *hematite* (Fe_2O_3), the more abundant, and *magnetite* (Fe_3O_4 , really $\text{FeO} \cdot \text{Fe}_2\text{O}_3$). *Taconite* ores contain iron oxides mixed with silicates and are more difficult to process than the others. However, taconite ores are being increasingly used as the more desirable ores are consumed.

To concentrate the iron in iron ores, advantage is taken of the natural magnetism of Fe_3O_4 (hence its name, *magnetite*). The Fe_3O_4 particles can be separated from the gangue by magnets. The ores that are not magnetic are often converted to Fe_3O_4 ; hematite is partially reduced to magnetite, while siderite is first converted to FeO thermally, then oxidized to Fe_2O_3 , and then reduced to Fe_3O_4 :



Sometimes the nonmagnetic ores are concentrated by flotation processes.

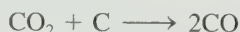
The most commonly used reduction process for iron takes place in the **blast furnace** (Fig. 21.36). The raw materials required are concentrated iron ore, coke, and limestone (which serves as a *flux* to trap impurities). The furnace, which is approximately 25 feet in diameter, is charged from the top with a mixture of iron ore, coke, and limestone. A very strong blast (~ 350 mi/h) of hot air is injected at the bottom, where the oxygen reacts with the carbon in the coke to form carbon monoxide, the reducing agent for the iron. The temperature of the charge increases as it travels down the furnace, with reduction of the iron to iron metal occurring in steps:



Iron can reduce carbon dioxide,



so complete reduction of the iron occurs only if the carbon dioxide is destroyed by adding excess coke:



The limestone (CaCO_3) in the charge loses carbon dioxide, or *calcines*, in the hot furnace and combines with silica and other impurities to form **slag**, which is mostly

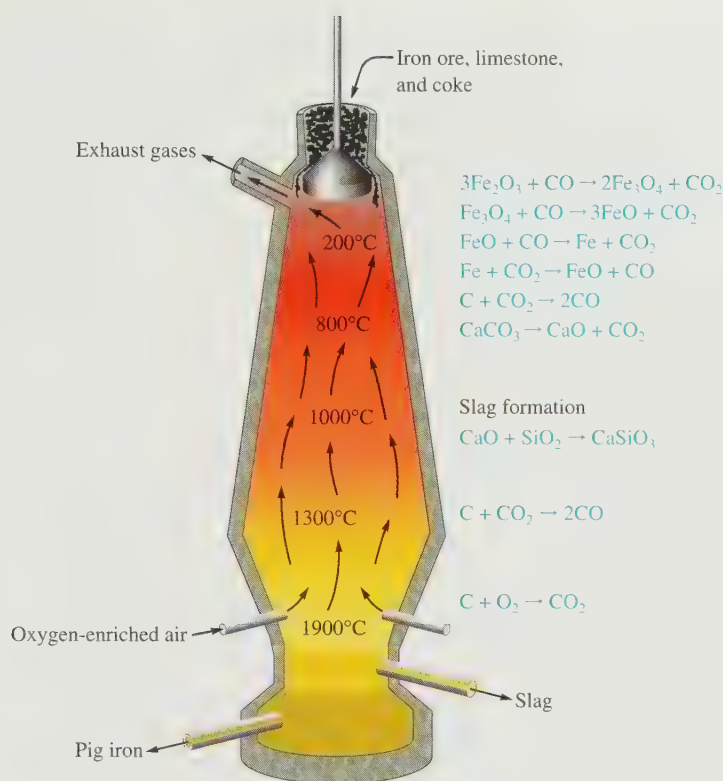
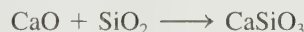


FIGURE 21.36
The blast furnace used in the production of iron.

molten calcium silicate, CaSiO_3 ,



and alumina (Al_2O_3). The slag floats on the molten iron and is skimmed off. The gas that escapes from the top of the furnace contains carbon monoxide, which is combined with air to form carbon dioxide. The energy released in this exothermic reaction is collected in a heat exchanger and used in heating the furnace.

The iron collected from the blast furnace, called **pig iron**, is quite impure. It contains ~90% iron, ~5% carbon, ~2% manganese, ~1% silicon, ~0.3% phosphorus, and ~0.04% sulfur (from impurities in the coke). The production of 1 ton of pig iron requires approximately 1.7 tons of iron ore, 0.5 ton of coke, 0.25 ton of limestone, and 2 tons of air.

Iron oxide also can be reduced in a **direct reduction furnace**, which operates at much lower temperatures (1300–2000°F) than a blast furnace and produces a solid “sponge iron” rather than molten iron. Because of the milder reaction conditions, the direct reduction furnace requires a higher grade of iron ore (with fewer impurities) than that used in a blast furnace. The iron from the direct reduction furnace is called *DRI* (*directly reduced iron*) and contains ~95% iron, with the balance mainly silica and alumina.

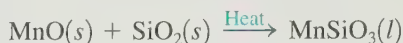
Production of Steel

Steel is an alloy and can be classified as **carbon steel**, which contains up to about 1.5% carbon, or **alloy steel**, which contains carbon plus other metals such as Cr, Co, Mn, and Mo. The wide range of mechanical properties associated with steel is

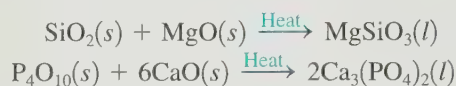
determined by its chemical composition and by the heat treatment of the final product.

The production of iron from its ore is fundamentally a reduction process, but the conversion of iron to steel is basically an oxidation process in which unwanted impurities are eliminated. Oxidation is carried out in various ways, but the two most common are the open hearth process and the basic oxygen process.

In the oxidation reactions of steelmaking, the manganese, phosphorus, and silicon in the impure iron react with oxygen to form oxides, which in turn react with appropriate fluxes to form slag. Sulfur enters the slag primarily as sulfides, and excess carbon forms carbon monoxide or carbon dioxide. The flux chosen depends on the major impurities present. If manganese is the chief impurity, an acidic flux of silica is used:



If the main impurity is silicon or phosphorus, a basic flux, usually lime (CaO) or magnesia (MgO), is needed to give reactions such as



Whether an acidic or a basic slag will be needed is a factor that must be considered when a furnace is constructed so that its refractory linings will be compatible with the slag. Silica bricks would deteriorate quickly in the presence of basic slag, and magnesia or lime bricks would dissolve in acid slag.

The **open hearth process** (Fig. 21.37) uses a dishlike container that holds 100 to 200 tons of molten iron. An external heat source is required to keep the iron molten, and a concave roof over the container reflects heat back toward the iron surface. A blast of air or oxygen is passed over the surface of the iron to react with impurities. Silicon and manganese are oxidized first and enter the slag, followed by oxidation of carbon to carbon monoxide, which causes agitation and foaming of the molten bath. The exothermic oxidation of carbon raises the temperature of the bath, causing the limestone flux to calcine:



The resulting lime floats to the top of the molten mixture (an event called the *lime boil*), where it combines with phosphates, sulfates, and silicates. Next comes the refining process, which involves continued oxidation of carbon and other impurities.

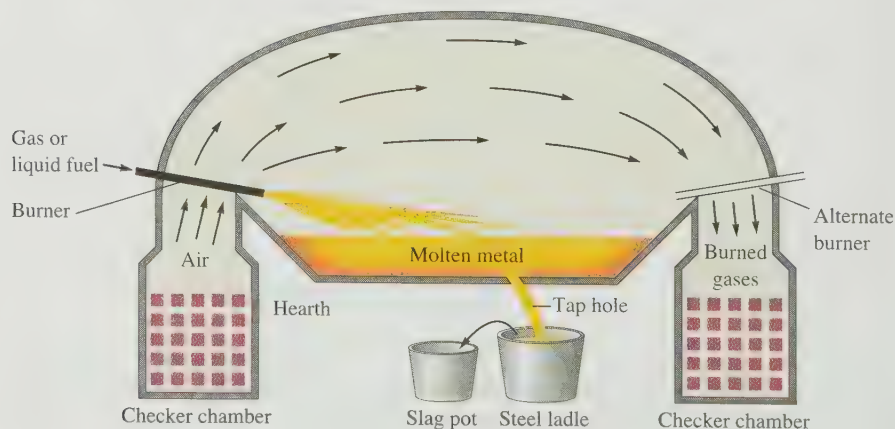


FIGURE 21.37

A schematic diagram of the open hearth process for steelmaking. The checker chambers contain bricks that absorb heat from gases passing over the molten charge. The flow of air and gases is reversed periodically.

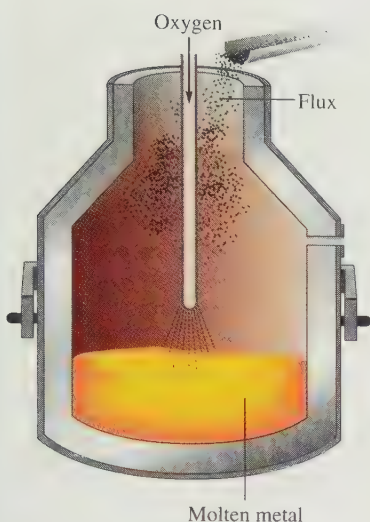
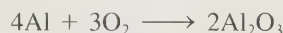


FIGURE 21.38
The basic oxygen process for steelmaking.

Refer to Section 10.3 for a review of packing and crystal lattices.

Because the melting point increases as the carbon content decreases, the bath temperatures must be increased during this phase of the operation. If the carbon content falls below that desired in the final product, coke or pig iron may be added.

The final composition of the steel is “fine-tuned” after the charge is poured. For example, aluminum is sometimes added at this stage to remove trace amounts of oxygen via the reaction



Alloying metals such as vanadium, chromium, titanium, manganese, and nickel are also added to give the steel the properties needed for a specific application.

The processing of a batch of steel by the open hearth process is quite slow, taking up to 8 hours. The **basic oxygen process** is much faster. Molten pig iron and scrap iron are placed in a barrel-shaped container (Fig. 21.38) that can hold as much as 300 tons of material. A high-pressure blast of oxygen is directed at the surface of the molten iron, oxidizing impurities in a manner very similar to that used in the open hearth process. Fluxes are added after the oxygen blow begins. One advantage of this process is that the exothermic oxidation reactions proceed so rapidly that they produce enough heat to raise the temperature nearly to the boiling point of iron without an external heat source. Also, at these high temperatures only about an hour is needed to complete the oxidation processes.

The **electric arc method**, which was once used only for small batches of specialty steels, is being utilized more and more in the steel industry. In this process an electric arc between carbon electrodes is used to melt the charge. This means that no fuel-borne impurities are added to the steel, since no fuel is needed. Also, higher temperatures are possible than in the open hearth or basic oxygen processes, and this leads to more effective removal of sulfur and phosphorus impurities. Oxygen is added in this process so that the oxide impurities in the steel can be controlled effectively.

Heat Treatment of Steel

One way of producing the desired physical properties in steel is by controlling the chemical composition (see Table 21.21). Another method for tailoring the properties of steel involves heat treatment. Pure iron exists in two different crystalline forms, depending on the temperature. At any temperature below 912°C, iron has a body-centered cubic structure and is called α -iron. Between 912°C and 1394°C, iron has a face-centered cubic structure called *austenite*, or γ -iron. At 1394°C, iron changes to δ -iron, a body-centered cubic structure identical to α -iron.

When iron is alloyed with carbon, which fits into holes among the iron atoms to form the interstitial alloy *carbon steel*, the situation becomes even more complex. For example, the temperature at which α -iron changes to austenite is lowered by about 200°C. Also, at high temperatures iron and carbon react by an endothermic reversible reaction to form an iron carbide called *cementite*:



By Le Châtelier’s principle, we can predict that cementite will become more stable relative to iron and carbon as the temperature is increased. This is the observed result.

Thus steel is really a mixture of iron metal in one of its crystal forms, carbon, and cementite. The proportions of these components are very important in determining the physical properties of steel.

TABLE 21.21 Percent Composition and Uses of Various Types of Steel

Type of Steel	% Carbon	% Manganese	% Phosphorus	% Sulfur	% Silicon	% Nickel	% Chromium	% Other	Uses
Plain carbon	≤1.35	≤1.65	≤0.04	≤0.05	≤0.60	—	—	—	Sheet steel, tools
High-strength (low-alloy)	≤0.25	≤1.65	≤0.04	≤0.05	0.15–0.9	0.4–1	0.3–1.3	Cu (0.2–0.6) Sb (0.01–0.08) V (0.01–0.08)	Transportation equipment, structural beams
Alloy	≤1.00	≤3.50	≤0.04	≤0.05	0.15–2.0	0.25–10.0	0.25–4.0	Mo (0.08–4.0) V (0–0.2) W (0–18) Co (0–5)	Automobile and aircraft engine parts
Stainless	0.03–1.2	1.0–10	0.04–0.06	≤0.03	1–3	1–22	4.0–27	—	Engine parts, steam turbine parts, kitchen utensils
Silicon	—	—	—	—	0.5–5.0	—	—	—	Electric motors and transformers

When steel is heated to temperatures in the region of 1000°C, much of the carbon is converted to cementite. If the steel is then allowed to cool slowly, the equilibrium shown above shifts to the left, and small crystals of carbon precipitate, giving a steel that is relatively ductile. If the cooling is very rapid, the equilibrium does not have time to adjust. The cementite is trapped, and the steel has a high cementite content, making it quite brittle. The proportions of carbon crystals and cementite can be “fine-tuned” to give the desired properties by heating to intermediate temperatures followed by rapid cooling, a process called **tempering**. The rate of heating and cooling determines not only the amounts of cementite present but also the size of its crystals and the form of crystalline iron present.

For Review

Summary

For the first-row transition metals (scandium through zinc), the last electrons occupy the 3*d* orbitals. Because electrons in these inner orbitals cannot participate as easily in bonding as can electrons in valence *s* and *p* orbitals, the chemistry of the transition elements is not greatly affected by the gradual change in the number of electrons. As a class, these elements have metallic physical and chemical properties. In forming ionic compounds with nonmetals, the transition metals exhibit several typical characteristics: More than one oxidation state is often found, the cations often are complex ions, and most compounds are colored and many are paramagnetic.

First-row transition metal ions can form a variety of ions by losing one or more of their electrons. The maximum possible oxidation state for a given element corresponds to the loss of all the 4*s* and 3*d* electrons, but toward the right end of the

Key Terms

Section 21.1

complex ion
first-row transition metals
lanthanide contraction
lanthanide series

Section 21.3

coordination compound
counterion
oxidation state

coordination number
ligand
coordinate covalent bond
monodentate (unidentate) ligand
chelating ligand (chelate)
bidentate ligand

Section 21.4

isomers
structural isomerism
stereoisomerism
coordination isomerism
linkage isomerism
geometrical (*cis-trans*) isomerism
trans isomer
cis isomer
optical isomerism
chiral
enantiomers

Section 21.6

crystal field model
d-orbital splitting
strong-field (low-spin) case
weak-field (high-spin) case
spectrochemical series

Section 21.7

cytochromes
heme
porphyrin
myoglobin
hemoglobin
carboxyhemoglobin

Section 21.8

metallurgy
minerals
gangue
flotation process
roasting
smelting
zone refining
pyrometallurgy
hydrometallurgy
leaching
cyanidation
blast furnace
slag
pig iron
direct reduction furnace
carbon steel
alloy steel
open hearth process
basic oxygen process
electric arc method
tempering

period the maximum possible oxidation state is not seen. Rather, $2+$ ions become the most common because the $3d$ electrons become increasingly difficult to remove.

Transition metals typically form coordination compounds, which consist of a complex ion (a transition metal ion with attached ligands) and counterions (anions or cations to produce a solid with no net charge). A ligand (a Lewis base) is a neutral molecule or ion having a lone pair of electrons that can be shared with an empty orbital on a metal ion (a Lewis acid) to form a coordinate covalent bond. The coordination number is the number of bonds formed by the metal ion to its ligands and can range from 2 to 8 depending on the size, charge, and electron configuration of the metal ion. A coordination number of 6 means an octahedral arrangement of ligands about the central metal ion; 2 means a linear arrangement, and 4 means either a planar or a tetrahedral arrangement.

Ligands can form one bond (unidentate), two bonds (bidentate), or as many as six bonds to the metal ion. Ligands that can bond to a metal ion through more than one atom are called chelates. For example, ethylenediamine (en) is bidentate, and EDTA is hexadentate (forms six bonds).

When two or more species have the same formula but different properties, they are called isomers. Structural isomers contain the same atoms but one or more different bonds. Coordination isomerism is a type of structural isomerism in which the composition of the coordination sphere around the metal varies. In linkage isomerism, the composition of the coordination spheres is the same, but the point of attachment of at least one of the ligands differs.

In stereoisomerism, the isomers have the same bonds but different spatial arrangements. For example, in geometric isomerism, atoms or groups can assume different relative positions in the coordination sphere around the metal. When two identical ligands lie across from each other, the isomer is *trans*; two ligands located next to each other produce the *cis* isomer.

A second type of stereoisomerism is optical isomerism, which is exhibited by molecules that have nonsuperimposable mirror images, that is, by chiral molecules. The pair of isomers, called enantiomers, rotate plane-polarized light in equal but opposite directions.

Bonding in complex ions can be described in terms of the localized electron model. However, even though this model can account for the bonding in complex ions by use of hybrid orbitals, it does not account for important properties such as magnetism and color. The crystal field model is much more successful at accounting for these properties by focusing on the energies of the d orbitals of the metal ion. To predict the effects ligands will have on the energies of the d orbitals, the ligands are approximated as negative point charges and the metal–ligand bonding is assumed to be completely ionic. The effect of the point charges in an octahedral complex ion is to split the $3d$ orbitals into two groups with different energies. If the splitting is large (the strong-field case), the electrons pair in the lower-energy orbitals before any jump the energy gap. If the splitting is small (the weak-field case), the electrons occupy all five d orbitals singly before pairing occurs. Ligands can be arranged according to their ability to produce splitting, in the spectrochemical series.

The crystal field model also accounts for the colors of complex ions. When a substance absorbs a certain wavelength of light in the visible region, its color is determined by the wavelengths of visible light that remain unabsorbed. Complex ions can absorb light as they transfer electrons between the split d orbitals. The relationship between the wavelength of light absorbed (λ) and the magnitude of the splitting (Δ) is given by

$$\Delta = \frac{hc}{\lambda}$$

Coordination complexes are vitally important in the chemistry of biologic systems, with iron having special importance in electron-transfer processes and the transport and storage of oxygen.

The process of separating a metal from its ore and preparing it for use is known as metallurgy. An ore is a mixture of minerals (relatively pure metal compounds) and gangue (sand, clay, and rock). Minerals can be concentrated by various methods before being processed. Minerals are often converted to the metal oxides (roasted) before the metal ion is reduced in a process called smelting.

Hydrometallurgy extracts metals from ores using aqueous chemical solutions in a process called leaching. An example of this is cyanidation, in which gold is leached with an aqueous cyanide solution.

Iron is often concentrated from iron ore by magnetic methods. The most commonly used reduction process for iron takes place in the blast furnace. The raw materials required are concentrated iron ore, coke, and limestone (which serves as a flux to trap impurities). The iron oxide (Fe_2O_3) is reduced by carbon monoxide to iron metal. The impure product, pig iron, is about 90% iron. Another process using the direct reduction furnace, which yields sponge iron, is coming into increased use.

Steel is a carbon-containing alloy of iron that is manufactured by oxidizing the impurities in pig iron or sponge iron in either the open hearth process or the basic oxygen process. Other metals are often added to form alloy steels.

In-Class Discussion Questions

These questions are designed to be considered by groups of students in class. Often these questions work well for introducing a particular topic in class.

1. You isolate a compound with the formula $\text{PtCl}_4 \cdot 2\text{KCl}$. From electrical conductance tests of an aqueous solution of the compound, you find that three ions per formula unit are present, and you also notice that addition of AgNO_3 does not cause a precipitate. Give the formula for this compound that shows the complex ion present. Explain your findings. Name this compound.
2. Both $\text{Ni}(\text{NH}_3)_4^{2+}$ and $\text{Ni}(\text{CN})_4^{2-}$ have four ligands. The first is paramagnetic, and the second is diamagnetic. Are the complex ions tetrahedral or square planar? Explain.
3. Which is more likely to be paramagnetic, $\text{Fe}(\text{CN})_6^{4-}$ or $\text{Fe}(\text{H}_2\text{O})_6^{2+}$? Explain.
4. A metal ion in a high-spin octahedral complex has two more unpaired electrons than the same ion does in a low-spin octahedral complex. Name some possible metal ions for which this would be true.

A blue question or exercise number indicates that the answer to that question or exercise appears at the back of this book and a solution appears in the *Solutions Guide*.

Questions

5. Define each of the following.
 - a. ligand
 - b. chelate
 - c. bidentate
 - d. complex ion
6. How would transition metal ions be classified using the Lewis definition of acids and bases? What must a ligand have to bond to a metal? What do we mean when we say that a bond is a coordinate covalent bond?
7. Define each of the following and give examples.
 - a. isomers
 - b. structural isomers
 - c. stereoisomers
 - d. coordination isomers
 - e. linkage isomers
 - f. geometrical isomers
 - g. optical isomers
8. Define each of the following.
 - a. weak-field ligand
 - b. strong-field ligand
 - c. low-spin complex
 - d. high-spin complex
9. Compounds of copper(II) are generally colored, but compounds of copper(I) are not. Explain. Would you expect $\text{Cd}(\text{NH}_3)_4\text{Cl}_2$ to be colored? Explain.
10. Compounds of Sc^{3+} are not colored, but those of Ti^{3+} and V^{3+} are. Explain.
11. Why are virtually all tetrahedral complexes “high spin”?
12. Why are CN^- and CO toxic to humans?
13. Oxalic acid is often used to remove rust stains. What properties of oxalic acid allow it to do this?
14. Why do transition metal ions often have several oxidation states, while representative metals generally have only one?

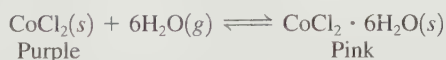
15. What is the lanthanide contraction? How does the lanthanide contraction affect the properties of the 4d and 5d transition metals?
16. Define and give an example of each of the following.
- roasting
 - smelting
 - flotation
 - leaching
 - gangue
17. What are the advantages and disadvantages of hydrometallurgy?
18. Describe the process by which a metal is purified by zone refining.

Exercises

In this section similar exercises are paired.

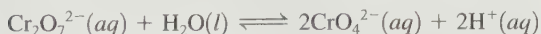
Transition Metals and Coordination Compounds

19. Write electron configurations for the following metals.
- Ni
 - Cd
 - Zr
 - Os
20. Write electron configurations for the following ions.
- Ni^{2+}
 - Cd^{2+}
 - Zr^{3+} and Zr^{4+}
 - Os^{2+} and Os^{3+}
21. Write electron configurations for each of the following.
- Ti, Ti^{2+} , Ti^{4+}
 - Re, Re^{2+} , Re^{3+}
 - Ir, Ir^{2+} , Ir^{3+}
22. Write electron configurations for each of the following.
- Cr, Cr^{2+} , Cr^{3+}
 - Cu, Cu^+ , Cu^{2+}
 - V, V^{2+} , V^{3+}
23. Novelty devices for predicting rain contain cobalt(II) chloride and are based on the following equilibrium:

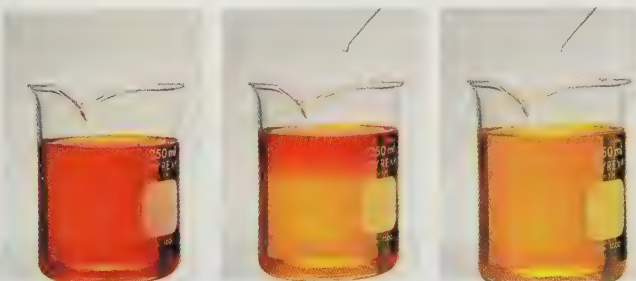


What color will such an indicator be if rain is imminent?

24. Chromium(VI) forms two different oxyanions, the orange dichromate ion, $\text{Cr}_2\text{O}_7^{2-}$, and the yellow chromate ion, CrO_4^{2-} . The equilibrium reaction between the two ions is

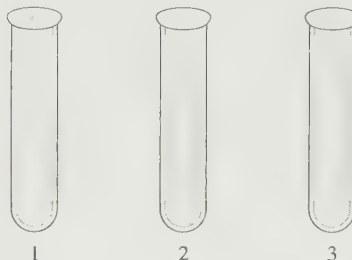


The following pictures show what happens when sodium hydroxide is added to a dichromate solution.



Explain what happened.

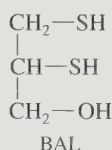
25. A series of chemicals was added to some $\text{AgNO}_3(aq)$. $\text{NaCl}(aq)$ was added first to the silver nitrate solution with the end result shown below in test tube 1, $\text{NH}_3(aq)$ was then added with the end result shown in test tube 2, and $\text{HNO}_3(aq)$ was added last with the end result shown in test tube 3.



Explain the results shown in each test tube. Include a balanced equation for the reaction(s) taking place.

26. When an aqueous solution of KCN is added to a solution containing Ni^{2+} ions, a precipitate forms, which redissolves on addition of more KCN solution. Write reactions describing what happens in this solution. (*Hint:* CN^- is a Brønsted–Lowry base [$K_b \approx 10^{-5}$] and a Lewis base.)
27. Consider aqueous solutions of the following coordination compounds: $\text{Co}(\text{NH}_3)_6\text{I}_3$, $\text{Pt}(\text{NH}_3)_4\text{I}_4$, Na_2PtI_6 , and $\text{Cr}(\text{NH}_3)_4\text{I}_3$. If aqueous AgNO_3 is added to separate beakers containing solutions of each coordination compound, how many moles of AgI will precipitate per mole of transition metal present? Assume that each transition metal ion forms an octahedral complex.
28. A coordination compound of cobalt(III) contains four ammonia molecules, one sulfate ion, and one chloride ion. Addition of aqueous BaCl_2 solution to an aqueous solution of the compound gives no precipitate. Addition of aqueous AgNO_3 to an aqueous solution of the compound produces a white precipitate. Propose a structure for this coordination compound.
29. Name the following complex ions.
- $\text{Ru}(\text{NH}_3)_5\text{Cl}^{2+}$
 - $\text{Fe}(\text{CN})_6^{4-}$
 - $\text{Mn}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_3^{2+}$
 - $\text{Co}(\text{NH}_3)_5\text{NO}_2^{2+}$
30. Name the following complex ions.
- $\text{Ni}(\text{CN})_4^{2-}$
 - $\text{Cr}(\text{NH}_3)_4\text{Cl}^+$
 - $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$
 - $\text{Co}(\text{SCN})_2(\text{H}_2\text{O})_4^+$
31. Name the following coordination compounds.
- $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2$
 - $[\text{Co}(\text{H}_2\text{O})_6]\text{I}_3$
 - $\text{K}_2[\text{PtCl}_4]$
 - $\text{K}_4[\text{PtCl}_6]$
 - $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$
 - $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$
32. Name the following coordination compounds.
- $[\text{Cr}(\text{H}_2\text{O})_5\text{Br}]\text{Br}_2$
 - $\text{Na}_3[\text{Co}(\text{CN})_6]$
 - $[\text{Fe}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_2(\text{NO}_2)_2]\text{Cl}$
 - $[\text{Pt}(\text{NH}_3)_4\text{I}_2][\text{PtI}_4]$

33. Give formulas for the following.
- potassium tetrachlorocobaltate(II)
 - aquatricarbonylplatinum(II) bromide
 - sodium dicyanobis(oxalato)ferrate(III)
 - triamminechloroethylenediaminechromium(III) iodide
34. Give formulas for the following complex ions.
- tetrachloroferrate(III) ion
 - pentaammineaquaruthenium(III) ion
 - tetracarbonyldihydroxochromium(III) ion
 - amminetrichloroplatinate(II) ion
35. Draw geometrical isomers of each of the following complex ions.
- $[\text{Co}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]^-$
 - $[\text{Pt}(\text{NH}_3)_4\text{I}_2]^{2+}$
 - $[\text{Ir}(\text{NH}_3)_3\text{Cl}_3]$
 - $[\text{Cr}(\text{en})(\text{NH}_3)_2\text{I}_2]^+$
36. Draw structures of each of the following.
- cis*-dichloroethylenediamineplatinum(II)
 - trans*-dichlorobis(ethylenediamine)cobalt(II)
 - cis*-tetraamminechloronitrocobalt(III) ion
 - trans*-tetraamminechloronitritocobalt(III) ion
 - trans*-diaquabis(ethylenediamine)copper(II) ion
37. Amino acids can act as ligands toward transition metal ions. The simplest amino acid is glycine ($\text{NH}_2\text{CH}_2\text{CO}_2\text{H}$). Draw a structure of the glycinate anion ($\text{NH}_2\text{CH}_2\text{CO}_2^-$) acting as a bidentate ligand. Draw the structural isomers of the square planar complex $\text{Cu}(\text{NH}_2\text{CH}_2\text{CO}_2)_2$.
38. BAL is a chelating agent used in treating heavy metal poisoning. It acts as a bidentate ligand. What type of linkage isomers are possible when BAL coordinates to a metal ion?

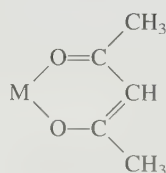


39. Which of the following ligands are capable of linkage isomerism? Explain your answer.



40. Draw all geometrical and linkage isomers of $\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2$.

41. Acetylacetone, abbreviated *acacH*, is a bidentate ligand. It loses a proton and coordinates as *acac*⁻, as shown below, where *M* is a transition metal:



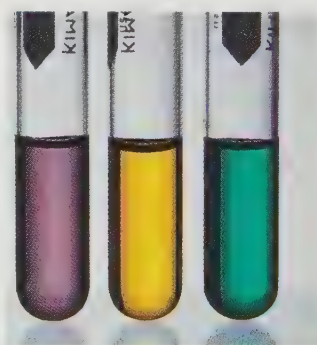
Which of the following complexes are optically active: *cis*- $\text{Cr}(\text{acac})_2(\text{H}_2\text{O})_2$, *trans*- $\text{Cr}(\text{acac})_2(\text{H}_2\text{O})_2$, and $\text{Cr}(\text{acac})_3$?

42. Draw all geometrical isomers of $\text{Pt}(\text{CN})_2\text{Br}_2(\text{H}_2\text{O})_2$. Which of these isomers has an optical isomer? Draw the various optical isomers.

Bonding, Color, and Magnetism in Coordination Compounds

43. Draw the *d*-orbital splitting diagrams for the octahedral complex ions of each of the following.
- Fe^{2+} (high and low spin)
 - Fe^{3+} (high spin)
 - Ni^{2+}
44. Draw the *d*-orbital splitting diagrams for the octahedral complex ions of each of the following.
- Zn^{2+}
 - Co^{2+} (high and low spin)
 - Ti^{3+}
45. The CrF_6^{4-} ion is known to have four unpaired electrons. Does the F^- ligand produce a strong or weak field?
46. The $\text{Co}(\text{NH}_3)_6^{3+}$ ion is diamagnetic, but $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ is paramagnetic. Explain.
47. How many unpaired electrons are in the following complex ions?
- $\text{Ru}(\text{NH}_3)_6^{2+}$ (low-spin case)
 - $\text{Ni}(\text{H}_2\text{O})_6^{2+}$
 - $\text{V}(\text{en})_3^{3+}$
48. The complex ion $\text{Fe}(\text{CN})_6^{3-}$ is paramagnetic with one unpaired electron. The complex ion $\text{Fe}(\text{SCN})_6^{3-}$ has five unpaired electrons. Where does SCN^- lie in the spectrochemical series relative to CN^- ?

49. The following test tubes each contain a different chromium complex ion.



For each compound, predict the predominant color of light absorbed. If the complex ions are $\text{Cr}(\text{NH}_3)_6^{3+}$, $\text{Cr}(\text{H}_2\text{O})_6^{3+}$, and $\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2^+$, what is the identity of the complex ion in each test tube? *Hint:* Reference the spectrochemical series.

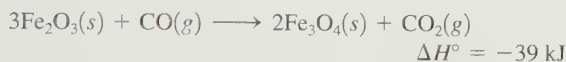
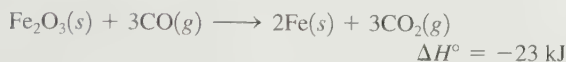
50. Consider the complex ions $\text{Co}(\text{NH}_3)_6^{3+}$, $\text{Co}(\text{CN})_6^{3-}$, and CoF_6^{3-} . The wavelengths of absorbed electromagnetic radiation for these compounds (in no specific order) are 770 nm, 440 nm, and 290 nm. Match the complex ion to the wavelength of absorbed electromagnetic radiation.

51. The wavelength of absorbed electromagnetic radiation for CoBr_4^{2-} is $3.4 \times 10^{-6} \text{ m}$. Will the complex ion CoBr_6^{4-} absorb electromagnetic radiation having a wavelength longer or shorter than $3.4 \times 10^{-6} \text{ m}$? Explain.
52. Tetrahedral complexes of Co^{2+} are quite common. Use a d -orbital splitting diagram to rationalize the stability of Co^{2+} tetrahedral complex ions.
53. How many unpaired electrons are present in the tetrahedral ion FeCl_4^{-} ?
54. The complex ion PdCl_4^{2-} is diamagnetic. Propose a structure for PdCl_4^{2-} .

Metallurgy

55. A blast furnace is used to reduce iron oxides to elemental iron. The reducing agent for this reduction process is carbon monoxide.

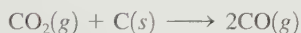
a. Given the following data:



determine ΔH° for the reaction

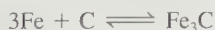


- b. The CO_2 produced in a blast furnace during the reduction process actually can oxidize iron into FeO . To eliminate this reaction, excess coke is added to convert CO_2 into CO by the reaction



Using data from Appendix 4, determine ΔH° and ΔS° for this reaction. Assuming ΔH° and ΔS° do not depend on temperature, at what temperature is the conversion reaction of CO_2 into CO spontaneous at standard conditions?

56. What roles do kinetics and thermodynamics play in the effect that the following reaction has on the properties of steel?



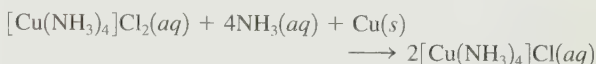
Additional Exercises

57. Ammonia and potassium iodide solutions are added to an aqueous solution of $\text{Cr}(\text{NO}_3)_3$. A solid is isolated (compound A), and the following data are collected:
- When 0.105 g of compound A was strongly heated in excess O_2 , 0.0203 g of CrO_3 was formed.
 - In a second experiment it took 32.93 mL of 0.100 M HCl to titrate completely the NH_3 present in 0.341 g of compound A.

- Compound A was found to contain 73.53% iodine by mass.
- The freezing point of water was lowered by 0.64°C when 0.601 g of compound A was dissolved in 10.00 g of H_2O ($K_f = 1.86^\circ\text{C} \cdot \text{kg/mol}$).

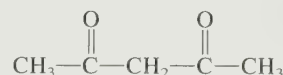
What is the formula of the compound? What is the structure of the complex ion present? (*Hints:* Cr^{3+} is expected to be six-coordinate, with NH_3 and possibly I^- as ligands. The I^- ions will be the counterions if needed.)

58. In the production of printed circuit boards for the electronics industry, a 0.60-mm layer of copper is laminated onto an insulating plastic board. Next, a circuit pattern made of a chemically resistant polymer is printed on the board. The unwanted copper is removed by chemical etching, and the protective polymer is finally removed by solvents. One etching reaction is



- Is this reaction an oxidation–reduction process? Explain.
 - A plant needs to manufacture 10,000 printed circuit boards, each $8.0 \times 16.0 \text{ cm}$ in area. An average of 80.% of the copper is removed from each board (density of copper = 8.96 g/cm^3). What masses of $[\text{Cu}(\text{NH}_3)_4]\text{Cl}_2$ and NH_3 are needed to do this? Assume 100% yield.
59. How many bonds could each of the following chelates form with a metal ion?

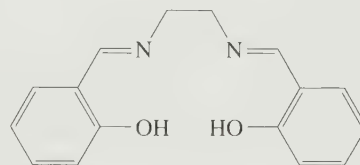
a. acetylacetone(acacH)



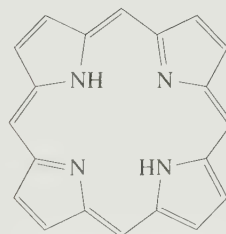
b. diethylenetriamine



c. salen



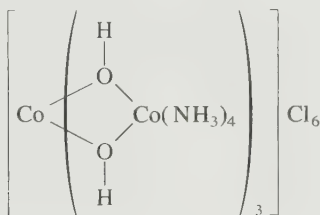
d. porphine



60. Until the discoveries of Werner, it was thought that carbon had to be present in a compound for it to be optically active.

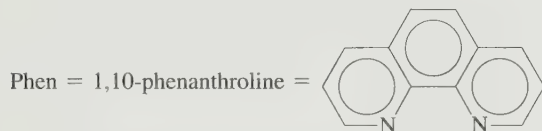
Werner prepared the following compound containing OH^- ions as bridging groups and separated the optical isomers.

- Draw structures of the two optically active isomers of this compound.
- What are the oxidation states of the cobalt ions?
- How many unpaired electrons are present if the complex is the low-spin case?

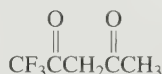


61. The complex ion $\text{Ru}(\text{phen})_3^{2+}$ has been used as a probe for the structure of DNA. (Phen is a bidentate ligand.)

- What type of isomerism is found in $\text{Ru}(\text{phen})_3^{2+}$?
- $\text{Ru}(\text{phen})_3^{2+}$ is diamagnetic (as are all complex ions of Ru^{2+}). Draw the crystal field diagram for the d orbitals in this complex ion.



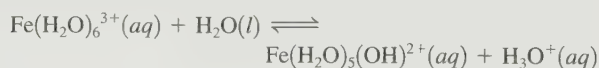
62. A compound related to acetylacetone is 1,1,1-trifluoroacetylacetone (abbreviated Htfa):



Htfa forms complexes in a manner similar to acetylacetone. (See Exercise 41.) Both Be^{2+} and Cu^{2+} form complexes with tfa^- having the formula $\text{M}(\text{tfa})_2$. Two isomers are formed for each metal complex.

- The Be^{2+} complexes are tetrahedral. Draw the two isomers of $\text{Be}(\text{tfa})_2$. What type of isomerism is exhibited by $\text{Be}(\text{tfa})_2$?
 - The Cu^{2+} complexes are square planar. Draw the two isomers of $\text{Cu}(\text{tfa})_2$. What type of isomerism is exhibited by $\text{Cu}(\text{tfa})_2$?
63. Would it be better to use octahedral Ni^{2+} complexes or octahedral Cr^{2+} complexes to determine whether a given ligand is a strong-field or weak-field ligand by measuring the number of unpaired electrons? How else could the relative ligand field strengths be determined?

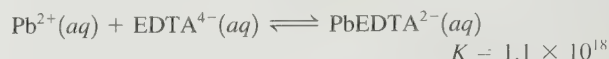
64. The equilibrium constant, K_a , for the reaction



is 6.0×10^{-3} .

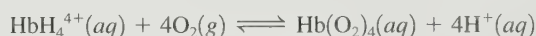
- Calculate the pH of a 0.10 M solution of $\text{Fe}(\text{H}_2\text{O})_6^{3+}$.
- Will a 1.0 M solution of iron(II) nitrate have a higher or lower pH than a 1.0 M solution of iron(III) nitrate? Explain.

65. Ethylenediaminetetraacetate (EDTA^{4-}) is used as a complexing agent in chemical analysis with the structure shown in Figure 21.7. Solutions of EDTA^{4-} are used to treat heavy metal poisoning by removing the heavy metal in the form of a soluble complex ion. The complex ion virtually eliminates the heavy metal ions from reacting with biochemical systems. The reaction of EDTA^{4-} with Pb^{2+} is



Consider a solution with 0.010 mol $\text{Pb}(\text{NO}_3)_2$ added to 1.0 L of an aqueous solution buffered at $\text{pH} = 13.00$ and containing 0.050 M Na_4EDTA . Does $\text{Pb}(\text{OH})_2$ precipitate from this solution? (K_{sp} for $\text{Pb}(\text{OH})_2 = 1.2 \times 10^{-15}$.)

66. Hemoglobin (abbreviated Hb) is a protein that is responsible for the transport of oxygen in the blood of mammals. Each hemoglobin molecule contains four iron atoms that serve as the binding sites for O_2 molecules. The oxygen binding is pH dependent. The relevant equilibrium reaction is



Use Le Châtelier's principle to answer the following.

- What form of hemoglobin, HbH_4^{4+} or $\text{Hb}(\text{O}_2)_4$, is favored in the lungs? What form is favored in the cells?
 - When a person hyperventilates, the concentration of CO_2 in the blood decreases. How does this affect the oxygen-binding equilibrium? How does breathing into a paper bag help to counteract this effect?
 - When a person has suffered a cardiac arrest, an injection of a sodium bicarbonate solution is given. Why is this step necessary?
67. Carbon monoxide is toxic because it binds more strongly to iron in hemoglobin (Hb) than does O_2 . Consider the following reactions and approximate standard free energy changes:

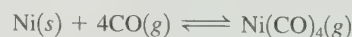


Using these data, estimate the equilibrium constant value at 25°C for the following reaction:



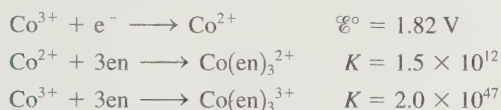
Challenge Problems

68. Impure nickel, refined by smelting sulfide ores in a blast furnace, can be converted into metal from 99.90% to 99.99% purity by the Mond process. The primary reaction involved in the Mond process is



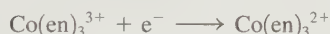
- Without referring to Appendix 4, predict the sign of ΔS° for the preceding reaction. Explain.

- b. The spontaneity of the preceding reaction is temperature dependent. Predict the sign of ΔS_{sur} for this reaction. Explain.
- c. For $\text{Ni}(\text{CO})_4(\text{g})$, $\Delta H_f^\circ = -607 \text{ kJ/mol}$ and $S^\circ = 417 \text{ J/K}\cdot\text{mol}$ at 298 K. Using these values and data in Appendix 4, calculate ΔH° and ΔS° for the preceding reaction.
- d. Calculate the temperature at which $\Delta G^\circ = 0$ ($K = 1$) for the preceding reaction, assuming that ΔH° and ΔS° do not depend on temperature.
- e. The first step of the Mond process involves equilibrating impure nickel with $\text{CO}(\text{g})$ and $\text{Ni}(\text{CO})_4(\text{g})$ at about 50°C . The purpose of this step is to convert as much nickel as possible into the gas phase. Calculate the equilibrium constant for the preceding reaction at 50°C .
- f. In the second step of the Mond process, the gaseous $\text{Ni}(\text{CO})_4$ is isolated and heated at 227°C . The purpose of this step is to deposit as much nickel as possible as pure solid (the reverse of the preceding reaction). Calculate the equilibrium constant for the above reaction at 227°C .
- g. Why is temperature increased for the second step of the Mond process?
69. Consider the following data:

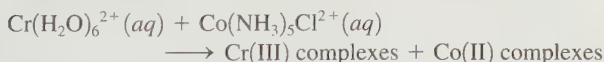


where en = ethylenediamine.

- a. Calculate $\mathcal{E}^\circ$ for the half-reaction

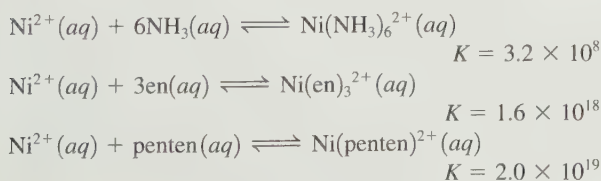


- b. Based on your answer to part a, which is the stronger oxidizing agent, Co^{3+} or $\text{Co}(\text{en})_3^{3+}$?
- c. Use the crystal field model to rationalize the result in part b.
70. Henry Taube, 1983 Nobel Prize winner in chemistry, has studied the mechanisms of the oxidation–reduction reactions of transition metal complexes. In one experiment he and his students studied the following reaction:

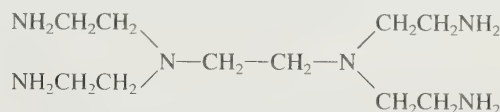


Chromium(III) and cobalt(III) complexes are substitutionally inert (no exchange of ligands) under conditions of the experiment. Chromium(II) and cobalt(II) complexes can exchange ligands very rapidly. One of the products of the reaction is $\text{Cr}(\text{H}_2\text{O})_5\text{Cl}^{2+}$. Is this consistent with the reaction proceeding through formation of $(\text{H}_2\text{O})_5\text{Cr}-\text{Cl}-\text{Co}(\text{NH}_3)_5$ as an intermediate? Explain.

71. Chelating ligands often form more stable complex ions than the corresponding monodentate ligands with the same donor atoms. For example,



where en is ethylenediamine and penten is



This increased stability is called the *chelate effect*. Based on bond energies, would you expect the enthalpy changes for the above reactions to be very different? What is the order (from least favorable to most favorable) of the entropy changes for the above reactions? How do the values of the formation constants correlate with ΔS° ? How can this be used to explain the chelate effect?

72. Qualitatively draw the crystal field splitting of the *d* orbitals in a trigonal planar complex ion. (Let the *z* axis be perpendicular to the plane of the complex.)
73. Qualitatively draw the crystal field splitting for a trigonal bipyramidal complex ion. (Let the *z* axis be perpendicular to the trigonal plane.)
74. a. Calculate the molar solubility of AgBr in pure water. K_{sp} for AgBr is 5.0×10^{-13} .
- b. Calculate the molar solubility of AgBr in 3.0 *M* NH_3 . The overall formation constant for $\text{Ag}(\text{NH}_3)_2^+$ is 1.7×10^7 , that is,
- $$\text{Ag}^+(\text{aq}) + 2\text{NH}_3(\text{aq}) \longrightarrow \text{Ag}(\text{NH}_3)_2^+(\text{aq})$$
- $$K = 1.7 \times 10^7.$$
- c. Compare the calculated solubilities from parts a and b. Explain any differences.
- d. What mass of AgBr will dissolve in 250.0 mL of 3.0 *M* NH_3 ?
- e. What effect does adding HNO_3 have on the solubilities calculated in parts a and b?

Marathon Problem

This problem is designed to incorporate several concepts and techniques into one situation. Marathon Problems can be used in class by groups of students to help facilitate problem-solving skills.

75. There are three salts that contain complex ions of chromium and have the molecular formula $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$. Treating 0.27 g of the first salt with a strong dehydrating agent resulted in a mass loss of 0.036 g. Treating 270 mg of the second salt with the same dehydrating agent resulted in a mass loss of 18 mg. The third salt did not lose any mass when treated with the same dehydrating agent. Addition of excess aqueous silver nitrate to 100.0-mL portions of 0.100 *M* solutions of each salt resulted in the formation of different masses of silver chloride; one solution yielded 1430 mg AgCl; another, 2870 mg AgCl; the third, 4300 mg AgCl. Two of the salts are green and one is violet.

Suggest probable structural formulas for these salts, defending your answer on the basis of the preceding observations. State which salt is most likely to be violet. Would a study of the magnetic properties of the salts be helpful in determining the structural formulas? Explain.



Media Activities

1. Chapter 21 discusses properties of transition metals with an emphasis on coordination compounds. For any coordination compound, make sure you can predict the structure, name the compound, draw possible isomers, and apply the crystal field model. Read the Overview on the student CD to review important topics in Chapter 21.
2. Open the Flame Tests Visualization on the student CD. The color of light in the various flame tests comes from the colors of visual light emitted as excited electrons drop down from higher to lower energy levels for the various ions. Notice that the compounds of copper used in the flame tests are colored [blue for copper (II) nitrate and green for copper (II) chloride],

while the other nontransitional metal compounds are white. Typically, transition metal complexes are colored.

One of the successes of the crystal field model is its ability to explain why transition metal complexes are colored. How does the crystal field model account for the colors of complex ions? Make sure you can do Exercises 21.44, 21.49, and 21.53, which refer to the crystal field model.

3. Test your understanding of Chapter 21 material by taking the ACE quizzes on the student web site.



For additional web activities and other resources, visit the Zumdahl, *Chemistry*, Sixth Edition textbook site at <http://chemistry.college.hmco.com/students>.

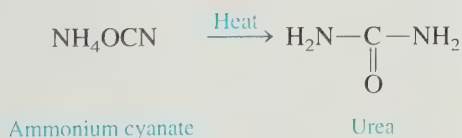


Organic and Biological Molecules

Two Group 4A elements, carbon and silicon, form the basis of most natural substances. Silicon, with its great affinity for oxygen, forms chains and rings containing Si—O—Si bridges to produce the silica and silicates that form the basis for most rocks, sands, and soils. What silicon is to the geological world, carbon is to the biological world. Carbon has the unusual ability of bonding strongly to itself to form long chains or rings of carbon atoms. In addition, carbon forms strong bonds to other nonmetals such as hydrogen, nitrogen, oxygen, sulfur, and the halogens. Because of these bonding properties, there are a myriad of carbon compounds; several million are now known, and the number continues to grow rapidly. Among these many compounds are the **biomolecules**, those responsible for maintaining and reproducing life.

The study of carbon-containing compounds and their properties is called **organic chemistry**. Although a few compounds involving carbon, such as its oxides and carbonates, are considered to be inorganic substances, the vast majority are organic compounds that typically contain chains or rings of carbon atoms.

Originally, the distinction between inorganic and organic substances was based on whether a compound was produced by living systems. For example, until the early nineteenth century it was believed that organic compounds had some sort of “life force” and could be synthesized only by living organisms. This view was dispelled in 1828 when the German chemist Friedrich Wöhler (1800–1882) prepared urea from the inorganic salt ammonium cyanate by simple heating:



CONTENTS

22.1 Alkanes: Saturated Hydrocarbons

- Isomerism in Alkanes
- Nomenclature
- Reactions of Alkanes
- Cyclic Alkanes

22.2 Alkenes and Alkynes

- Reactions of Alkenes and Alkynes

22.3 Aromatic Hydrocarbons

22.4 Hydrocarbon Derivatives

- Alcohols
- Aldehydes and Ketones
- Carboxylic Acids and Esters
- Amines

22.5 Polymers

- The Development and Properties of Polymers
- Types of Polymers
- Polymers Based on Ethylene

22.6 Natural Polymers

- Proteins
- Carbohydrates
- Nucleic Acids

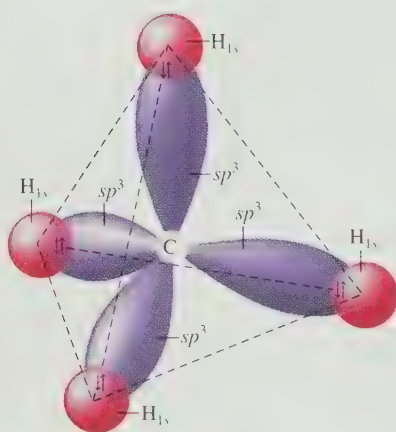


FIGURE 22.1
The C—H bonds in methane.

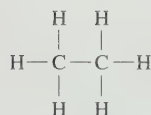
Urea is a component of urine, so it is clearly an organic material; yet here was clear evidence that it could be produced in the laboratory as well as by living things.

Organic chemistry plays a vital role in our quest to understand living systems. Beyond that, the synthetic fibers, plastics, artificial sweeteners, and drugs that are such an accepted part of modern life are products of industrial organic chemistry. In addition, the energy on which we rely so heavily to power our civilization is based mostly on the organic materials found in coal and petroleum.

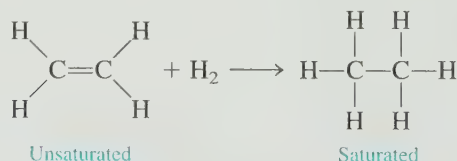
Because organic chemistry is such a vast subject, we can provide only a brief introduction to it in this book. We will begin with the simplest class of organic compounds, the hydrocarbons, and then show how most other organic compounds can be considered to be derivatives of hydrocarbons.

22.1 Alkanes: Saturated Hydrocarbons

As the name indicates, **hydrocarbons** are compounds composed of carbon and hydrogen. Those compounds whose carbon–carbon bonds are all single bonds are said to be **saturated**, because each carbon is bound to four atoms, the maximum number. Hydrocarbons containing carbon–carbon multiple bonds are described as being **unsaturated**, since the carbon atoms involved in a multiple bond can react with additional atoms, as shown by the *addition* of hydrogen to ethylene:



(a)



Note that each carbon in ethylene is bonded to three atoms (one carbon and two hydrogens) but that each can bond to one additional atom if one bond of the carbon–carbon double bond is broken.

The simplest member of the saturated hydrocarbons, which are also called the **alkanes**, is *methane* (CH_4). As discussed in Section 9.1, methane has a tetrahedral structure and can be described in terms of a carbon atom using an sp^3 hybrid set of orbitals to bond to the four hydrogen atoms (see Fig. 22.1). The next alkane, the one containing two carbon atoms, is *ethane* (C_2H_6), as shown in Fig. 22.2. Each carbon in ethane is surrounded by four atoms and thus adopts a tetrahedral arrangement and sp^3 hybridization, as predicted by the localized electron model.

The next two members of the series are *propane* (C_3H_8) and *butane* (C_4H_{10}), shown in Fig. 22.3. Again, each carbon is bonded to four atoms and is described as sp^3 hybridized.

Alkanes in which the carbon atoms form long “strings” or chains are called **normal**, **straight-chain**, or **unbranched hydrocarbons**. As can be seen from Fig. 22.3, the chains in normal alkanes are not really straight but zig-zag, since the tetrahedral C—C—C angle is 109.5° . The normal alkanes can be represented by the structure



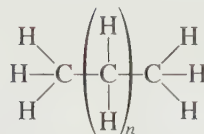
FIGURE 22.2
(a) The Lewis structure of ethane (C_2H_6). (b) The molecular structure of ethane represented by space-filling and ball-and-stick models.

FIGURE 22.3

The structures of (a) propane ($\text{CH}_3\text{CH}_2\text{CH}_3$) and (b) butane ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$). Each angle shown in red is 109.5° .

(a)

(b)



where n is an integer. Note that each member is obtained from the previous one by inserting a *methylene* (CH_2) group. We can condense the structural formulas by omitting some of the C—H bonds. For example, the general formula for normal alkanes shown above can be condensed to



The first ten normal alkanes and some of their properties are listed in Table 22.1. Note that all alkanes can be represented by the general formula $\text{C}_n\text{H}_{2n+2}$. For example, nonane, which has nine carbon atoms, is represented by $\text{C}_9\text{H}_{(2 \times 9) + 2}$, or C_9H_{20} . Also note from Table 22.1 that the melting points and boiling points increase as the molar masses increase, as we would expect.

Isomerism in Alkanes

Butane and all succeeding members of the alkanes exhibit **structural isomerism**. Recall from Section 21.4 that structural isomerism occurs when two molecules have the same atoms but different bonds. For example, butane can exist as a straight-chain molecule (normal butane, or *n*-butane) or with a branched-chain structure (called isobutane), as shown in Fig. 22.4. Because of their different structures, these molecules exhibit different properties. For example, the boiling point of *n*-butane is -0.5°C , whereas that of isobutane is -12°C .

TABLE 22.1 Selected Properties of the First Ten Normal Alkanes

Name	Formula	Molar Mass	Melting Point ($^\circ\text{C}$)	Boiling Point ($^\circ\text{C}$)	Number of Structural Isomers
Methane	CH_4	16	-182	-162	1
Ethane	C_2H_6	30	-183	-89	1
Propane	C_3H_8	44	-187	-42	1
Butane	C_4H_{10}	58	-138	0	2
Pentane	C_5H_{12}	72	-130	36	3
Hexane	C_6H_{14}	86	-95	68	5
Heptane	C_7H_{16}	100	-91	98	9
Octane	C_8H_{18}	114	-57	126	18
Nonane	C_9H_{20}	128	-54	151	35
Decane	$\text{C}_{10}\text{H}_{22}$	142	-30	174	75

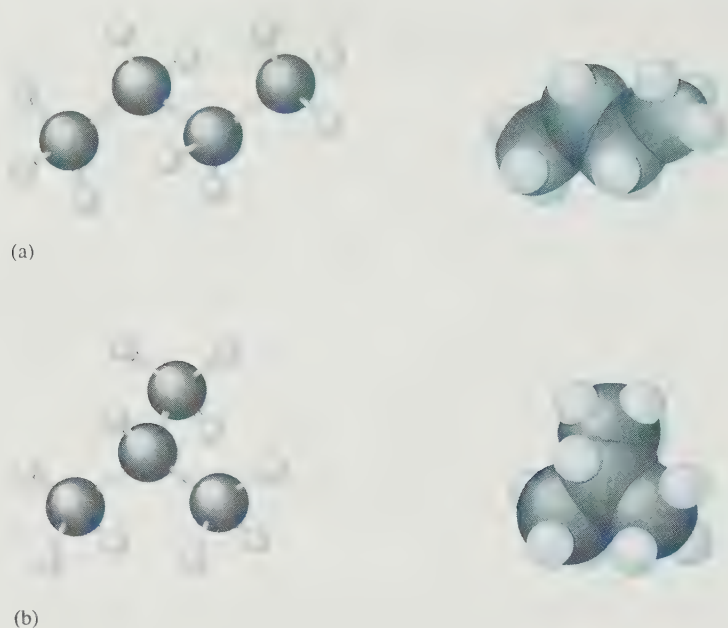


FIGURE 22.4
 (a) Normal butane (abbreviated *n*-butane). (b) The branched isomer of butane (called isobutane).

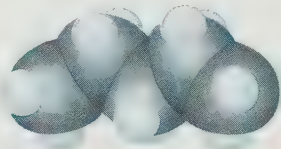
SAMPLE EXERCISE 22.1

Structural Isomerism

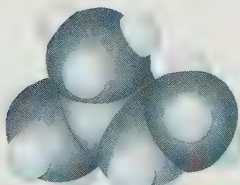
Draw the isomers of pentane.

SOLUTION

Pentane (C_5H_{12}) has the following isomeric structures:

- 

$$CH_3-CH_2-CH_2-CH_2-CH_3$$

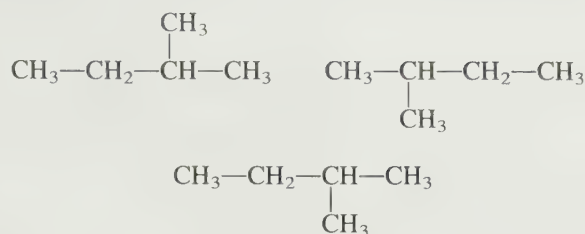
n-Pentane
- 

$$\begin{array}{c} CH_3 \\ | \\ CH_3-CH-CH_2-CH_3 \end{array}$$

Isopentane
- 

$$\begin{array}{c} CH_3 \\ | \\ CH_3-C-CH_3 \\ | \\ CH_3 \end{array}$$

Neopentane



which might appear to be other isomers, are actually identical to structure 2.

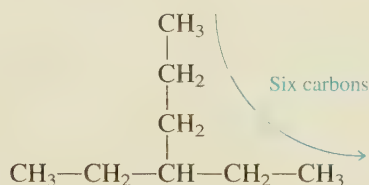
See Exercise 22.23.

Nomenclature

Because there are literally millions of organic compounds, it would be impossible to remember common names for all of them. We must have a systematic method for naming them. The following rules are used in naming alkanes.

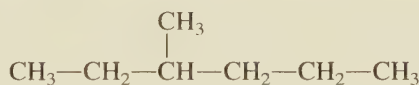
Rules for Naming Alkanes

1. The names of the alkanes beyond butane are obtained by adding the suffix *-ane* to the Greek root for the number of carbon atoms (*pent-* for five, *hex-* for six, and so on). For a branched hydrocarbon, the longest continuous chain of carbon atoms determines the root name for the hydrocarbon. For example, in the alkane



the longest chain contains six carbon atoms, and this compound is named as a hexane.

2. When alkane groups appear as substituents, they are named by dropping the *-ane* and adding *-yl*. For example, $-\text{CH}_3$ is obtained by removing a hydrogen from methane and is called *methyl*, $-\text{C}_2\text{H}_5$ is called *ethyl*, $-\text{C}_3\text{H}_7$ is called *propyl*, and so on. The compound above is therefore an ethylhexane. (See Table 22.2.)
3. The positions of substituent groups are specified by numbering the longest chain of carbon atoms sequentially, starting at the end closest to the branching. For example, the compound



1	2	3	4	5	6	Correct numbering
6	5	4	3	2	1	Incorrect numbering

is called 3-methylhexane. Note that the top set of numbers is correct since the left end of the molecule is closest to the branching, and this gives the smallest number for the position of the substituent. Also, note that a hyphen is written between the number and the substituent name.

4. The location and name of each substituent are followed by the root alkane name. The substituents are listed in alphabetical order, and the prefixes *di-*, *tri-*, and so on, are used to indicate multiple, identical substituents.

TABLE 22.2
The Most Common Alkyl
Substituents and Their Names

Structure*	Name†
$-\text{CH}_3$	Methyl
$-\text{CH}_2\text{CH}_3$	Ethyl
$-\text{CH}_2\text{CH}_2\text{CH}_3$	Propyl
$\begin{array}{c} \\ \text{CH}_3\text{CHCH}_3 \end{array}$	Isopropyl
$-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	Butyl
$\begin{array}{c} \\ \text{CH}_3\text{CHCH}_2\text{CH}_3 \end{array}$	sec-Butyl
$\begin{array}{c} \text{H} \\ \\ -\text{CH}_2-\text{C}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	Isobutyl
$\begin{array}{c} \text{CH}_3 \\ \\ -\text{C}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	tert-Butyl

* The bond with one end open shows the point of attachment of the substituent to the carbon chain.

†For the butyl groups, *sec-* indicates attachment to the chain through a secondary carbon, a carbon atom attached to two other carbon atoms. The designation *tert-* signifies attachment through a tertiary carbon, a carbon attached to three other carbon atoms.

SAMPLE EXERCISE 22.2

Isomerism and Nomenclature

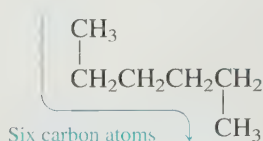
Draw the structural isomers for the alkane C_6H_{14} and give the systematic name for each one.

SOLUTION

We will proceed systematically, starting with the longest chain and then rearranging the carbons to form the shorter, branched chains.

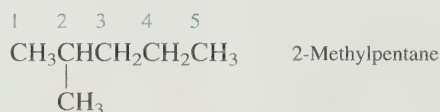
1. $CH_3CH_2CH_2CH_2CH_2CH_3$ Hexane

Note that although a structure such as



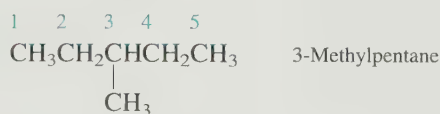
may look different it is still hexane, since the longest carbon chain has six atoms.

2. We now take one carbon out of the chain and make it a methyl substituent.



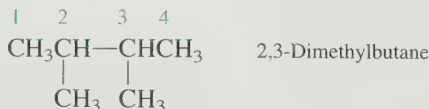
Since the longest chain consists of five carbons, this is a substituted pentane: 2-methylpentane. The 2 indicates the position of the methyl group on the chain. Note that if we numbered the chain from the right end, the methyl group would be on carbon 4. Because we want the smallest possible number, the numbering shown is correct.

3. The methyl substituent can also be on carbon 3 to give



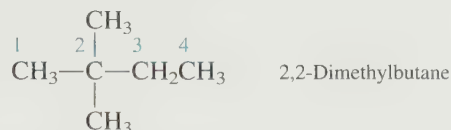
Note that we have now exhausted all possibilities for placing a single methyl group on pentane.

4. Next, we can take two carbons out of the original six-member chain:

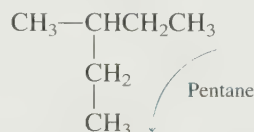


Since the longest chain now has four carbons, the root name is butane. Since there are two methyl groups, we use the prefix *di*-. The numbers denote that the two methyl groups are positioned on the second and third carbons in the butane chain. Note that when two or more numbers are used, they are separated by a comma.

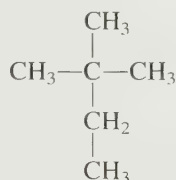
5. The two methyl groups can also be attached to the same carbon atom as shown here:



We might also try ethyl-substituted butanes, such as



However, note that this is instead a pentane (3-methylpentane), since the longest chain has five carbon atoms. Thus it is not a new isomer. Trying to reduce the chain to three atoms provides no further isomers either. For example, the structure



is actually 2,2-dimethylbutane.

Thus there are only five distinct structural isomers of C_6H_{14} : hexane, 2-methylpentane, 3-methylpentane, 2,3-dimethylbutane, and 2,2-dimethylbutane.

See Exercises 22.25 and 22.26.

SAMPLE EXERCISE 22.3

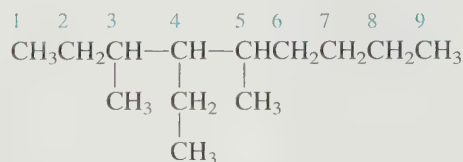
Structures from Names

Determine the structure for each of the following compounds.

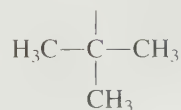
- a. 4-ethyl-3,5-dimethylnonane b. 4-*tert*-butylheptane

SOLUTION

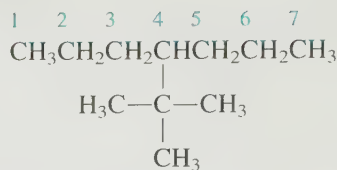
- a. The root name *nonane* signifies a nine-carbon chain. Thus we have



- b. Heptane signifies a seven-carbon chain, and the *tert*-butyl group is



Thus we have



See Exercises 22.27 and 22.28.

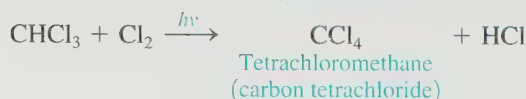
Reactions of Alkanes

Because they are saturated compounds and because the C—C and C—H bonds are relatively strong, the alkanes are fairly unreactive. For example, at 25°C they do not react with acids, bases, or strong oxidizing agents. This chemical inertness makes them valuable as lubricating materials and as the backbone for structural materials such as plastics.

At a sufficiently high temperature alkanes do react vigorously and exothermically with oxygen, and these **combustion reactions** are the basis for their widespread use as fuels. For example, the reaction of butane with oxygen is



The alkanes can also undergo **substitution reactions**, primarily where halogen atoms replace hydrogen atoms. For example, methane can be successively chlorinated as follows:



The $h\nu$ above the arrow represents ultraviolet light.



A butane lighter used for camping.

Note that the products of the last two reactions have two names; the systematic name is given first, followed by the common name in parentheses. (This format will be used throughout this chapter for compounds that have common names.) Also, note that ultraviolet light ($h\nu$) furnishes the energy to break the Cl—Cl bond to produce chlorine atoms:



A chlorine atom has an unpaired electron, as indicated by the dot, which makes it very reactive and able to attack the C—H bond.

Substituted methanes with the general formula $\text{CF}_x\text{Cl}_{4-x}$ containing both chlorine and fluorine as substituents are called chlorofluorocarbons (CFCs) and are also known as *Freons*. These substances are very unreactive and have been extensively used as coolant fluids in refrigerators and air conditioners. Unfortunately, their chemical inertness allows Freons to remain in the atmosphere so long that they eventually

reach altitudes where they are a threat to the protective ozone layer (see Section 12.8), and the use of these compounds is being rapidly phased out.

Alkanes can also undergo **dehydrogenation reactions** in which hydrogen atoms are removed and the product is an unsaturated hydrocarbon. For example, in the presence of chromium(III) oxide at high temperatures, ethane can be dehydrogenated, yielding ethylene:

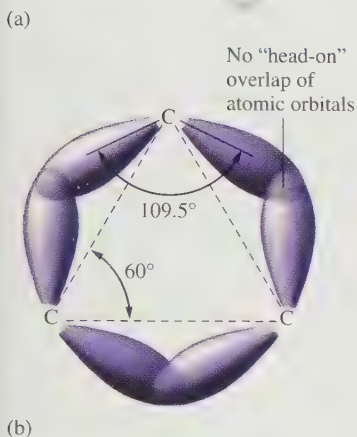
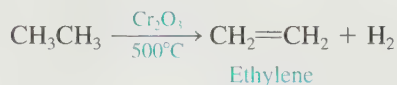


FIGURE 22.5

(a) The molecular structure of cyclopropane (C_3H_6). (b) The overlap of the sp^3 orbitals that form the C—C bonds in cyclopropane.

Cyclic Alkanes

Besides forming chains, carbon atoms also form rings. The simplest of the **cyclic alkanes** (general formula C_nH_{2n}) is cyclopropane (C_3H_6), shown in Fig. 22.5(a). Since the carbon atoms in cyclopropane form an equilateral triangle with 60° bond angles, their sp^3 hybrid orbitals do not overlap head-on as in normal alkanes [Fig. 22.5(b)]. This results in unusually weak, or *strained*, C—C bonds; thus the cyclopropane molecule is much more reactive than straight-chain propane. The carbon atoms in cyclobutane (C_4H_8) form a square with 88° bond angles, and cyclobutane is also quite reactive.

The next two members of the series, cyclopentane (C_5H_{10}) and cyclohexane (C_6H_{12}), are quite stable, because their rings have bond angles very close to the tetrahedral angles, which allows the sp^3 hybrid orbitals on adjacent carbon atoms to overlap head-on and form normal C—C bonds, which are quite strong. To attain the tetrahedral angles, the cyclohexane ring must "pucker"—that is, become nonplanar. Cyclohexane can exist in two forms, the *chair* and the *boat* forms, are shown in Fig. 22.6. The two hydrogen atoms above the ring in the boat form are quite close to each other, and the resulting repulsion between these atoms causes the chair form to be preferred. At 25°C more than 99% of cyclohexane exists in the chair form.

For simplicity, the cyclic alkanes are often represented by the following structures:

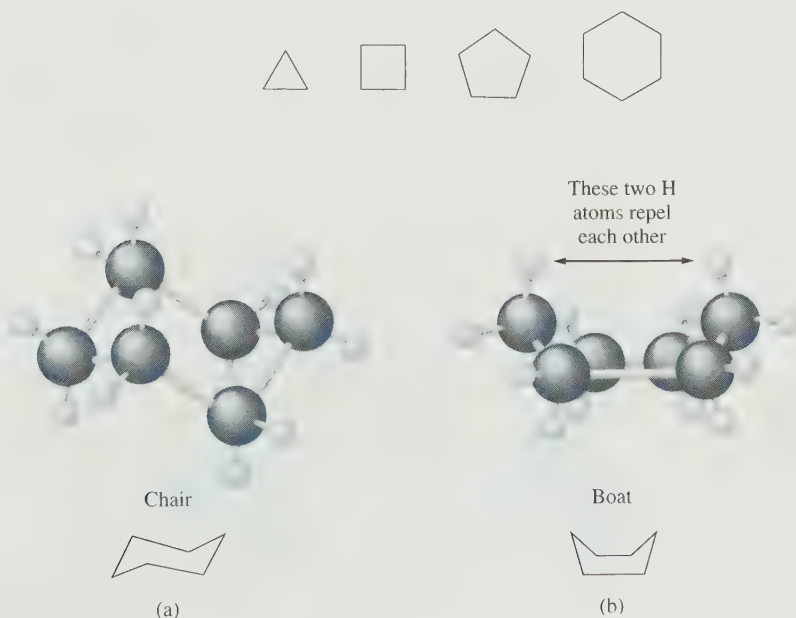


FIGURE 22.6

The (a) chair and (b) boat forms of cyclohexane.

Thus the structure



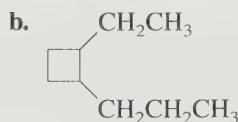
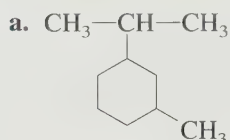
represents methylcyclopropane.

The nomenclature for cycloalkanes follows the same rules as for the other alkanes except that the root name is preceded by the prefix *cyclo-*. The ring is numbered to yield the smallest substituent numbers possible.

SAMPLE EXERCISE 22.4

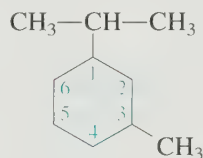
Naming Cyclic Alkanes

Name each of the following cyclic alkanes.



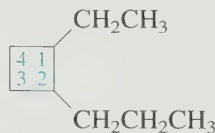
SOLUTION

a. The six-carbon cyclohexane ring is numbered as follows:



There is an isopropyl group at carbon 1 and a methyl group at carbon 3. The name is 1-isopropyl-3-methylcyclohexane, since the alkyl groups are named in alphabetical order.

b. This is a cyclobutane ring, which is numbered as follows:

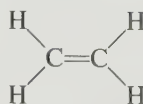


The name is 1-ethyl-2-propylcyclobutane.

See Exercise 22.30.

22.2 Alkenes and Alkynes

Multiple carbon–carbon bonds result when hydrogen atoms are removed from alkanes. Hydrocarbons that contain at least one carbon–carbon double bond are called **alkenes** and have the general formula C_nH_{2n} . The simplest alkene (C_2H_4), commonly known as *ethylene*, has the Lewis structure



As discussed in Section 9.1, each carbon in ethylene can be described as sp^2 hybridized. The C–C σ bond is formed by sharing an electron pair between sp^2

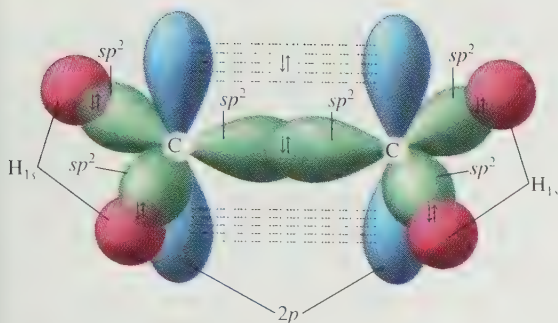


FIGURE 22.7
The bonding in ethylene.

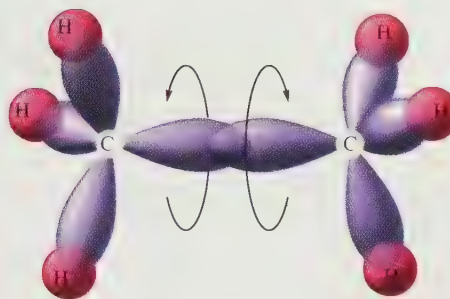


FIGURE 22.8
The bonding in ethane.

orbitals, and the π bond is formed by sharing a pair of electrons between p orbitals (Fig. 22.7).

The systematic nomenclature for alkenes is quite similar to that for alkanes.

1. The root hydrocarbon name ends in *-ene* rather than *-ane*. Thus the systematic name for C_2H_4 is *ethene* and the name for C_3H_6 is *propene*.
2. In alkenes containing more than three carbon atoms, the location of the double bond is indicated by the lowest-numbered carbon atom involved in the bond. Thus $\text{CH}_2=\text{CHCH}_2\text{CH}_3$ is called 1-butene, and $\text{CH}_3\text{CH}=\text{CHCH}_3$ is called 2-butene.

Note from Fig. 22.7 that the p orbitals on the two carbon atoms in ethylene must be lined up (parallel) to allow formation of the π bond. This prevents rotation of the two CH_2 groups relative to each other at ordinary temperatures, in contrast to alkanes, where free rotation is possible (see Fig. 22.8). The restricted rotation around doubly bonded carbon atoms means that alkenes exhibit **cis-trans isomerism**. For example, there are two stereoisomers of 2-butene (Fig. 22.9). Identical substituents on the same side of the double bond are designated *cis* and those on opposite sides are labeled *trans*.

Alkynes are unsaturated hydrocarbons containing at least one triple carbon-carbon bond. The simplest alkyne is C_2H_2 (commonly called *acetylene*), which has the systematic name *ethyne*. As discussed in Section 9.1, the triple bond in acetylene can be described as one σ bond between two sp hybrid orbitals on the two carbon atoms and two π bonds involving two $2p$ orbitals on each carbon atom (Fig. 22.10).

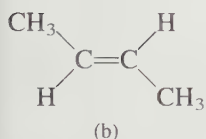
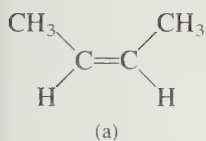


FIGURE 22.9
The two stereoisomers of 2-butene: (a) *cis*-2-butene and (b) *trans*-2-butene.

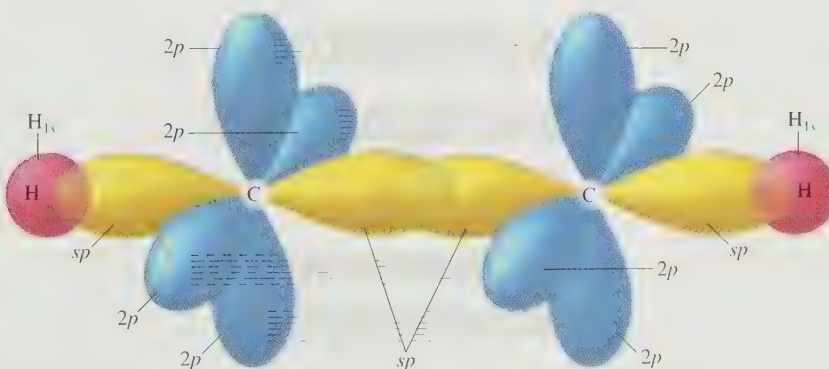
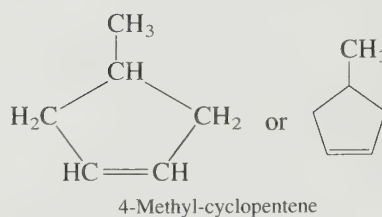
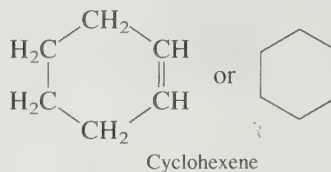


FIGURE 22.10
The bonding in acetylene.

The nomenclature for alkynes involves the use of *-yne* as a suffix to replace the *-ane* of the parent alkane. Thus the molecule $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CCH}_3$ has the name 2-pentyne.

Like alkanes, unsaturated hydrocarbons can exist as ringed structures, for example,

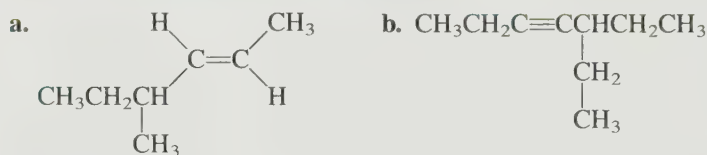
For cyclic alkenes, number through the double bond toward the substituent.



SAMPLE EXERCISE 22.5

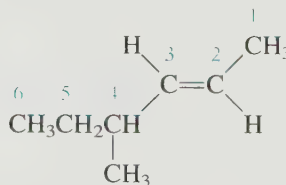
Naming Alkenes and Alkynes

Name each of the following molecules.



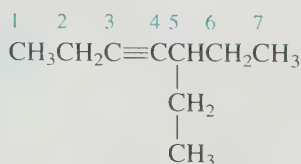
SOLUTION

a. The longest chain, which contains six carbon atoms, is numbered as follows:



Thus the hydrocarbon is a 2-hexene. Since the hydrogen atoms are located on opposite sides of the double bond, this molecule corresponds to the *trans* isomer. The name is 4-methyl-*trans*-2-hexene.

b. The longest chain, consisting of seven carbon atoms, is numbered as shown (giving the triple bond the lowest possible number):





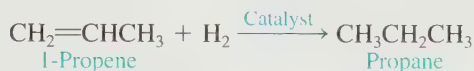
A worker using an oxyacetylene torch.

The hydrocarbon is a 3-heptyne. The full name is 5-ethyl-3-heptyne, where the position of the triple bond is indicated by the lower-numbered carbon atom involved in this bond.

See Exercises 22.31 through 22.34, 22.47, and 22.48.

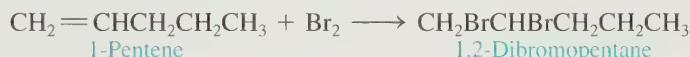
Reactions of Alkenes and Alkynes

Because alkenes and alkynes are unsaturated, their most important reactions are **addition reactions**. In these reactions π bonds, which are weaker than the C—C σ bonds, are broken, and new σ bonds are formed to the atoms being added. For example, **hydrogenation reactions** involve the addition of hydrogen atoms:



For this reaction to proceed rapidly at normal temperatures, a catalyst of platinum, palladium, or nickel is used. The catalyst serves to help break the relatively strong H—H bond, as was discussed in Section 12.8. Hydrogenation of alkenes is an important industrial process, particularly in the manufacture of solid shortenings where unsaturated fats (fats containing double bonds), which are generally liquid, are converted to solid saturated fats.

Halogenation of unsaturated hydrocarbons involves addition of halogen atoms. For example,



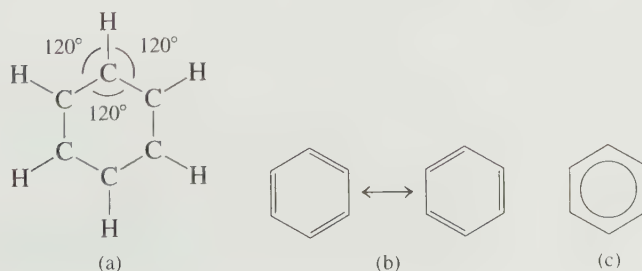
Another important reaction involving certain unsaturated hydrocarbons is **polymerization**, a process in which many small molecules are joined together to form a large molecule. Polymerization will be discussed in Section 22.5.

22.3 Aromatic Hydrocarbons

A special class of cyclic unsaturated hydrocarbons is known as the **aromatic hydrocarbons**. The simplest of these is benzene (C_6H_6), which has a planar ring structure, as shown in Fig. 22.11(a). In the localized electron model of the bonding in benzene, resonance structures of the type shown in Fig. 22.11(b) are used to account for the known equivalence of all the carbon—carbon bonds. But as we discussed in Section 9.5, the best description of the benzene molecule assumes that sp^2 hybrid orbitals on each carbon are used to form the C—C and C—H σ bonds, while the

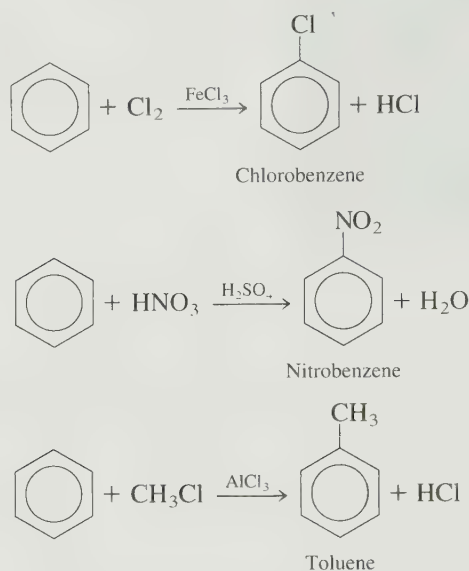
FIGURE 22.11

(a) The structure of benzene, a planar ring system in which all bond angles are 120° . (b) Two of the resonance structures of benzene. (c) The usual representation of benzene. The circle represents the electrons in the delocalized π system. All C—C bonds in benzene are equivalent.



remaining $2p$ orbital on each carbon is used to form π molecular orbitals. The delocalization of these π electrons is usually indicated by a circle inside the ring [Fig. 22.11(c)].

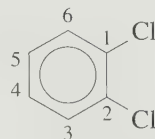
The delocalization of the π electrons makes the benzene ring behave quite differently from a typical unsaturated hydrocarbon. As we have seen previously, unsaturated hydrocarbons generally undergo rapid addition reactions. However, benzene does not. Instead, it undergoes substitution reactions in which *hydrogen atoms are replaced by other atoms*. For example,



In each case the substance shown over the arrow is needed to catalyze these substitution reactions.

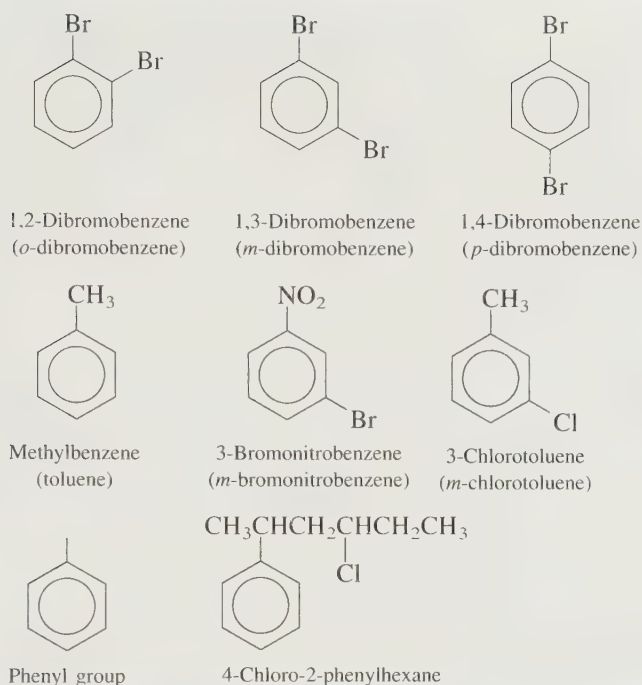
Substitution reactions are characteristic of saturated hydrocarbons, and addition reactions are characteristic of unsaturated ones. The fact that benzene reacts more like a saturated hydrocarbon indicates the great stability of the delocalized π electron system.

The nomenclature of benzene derivatives is similar to the nomenclature for saturated ring systems. If there is more than one substituent present, numbers are used to indicate substituent positions. For example, the compound



is named 1,2-dichlorobenzene. Another nomenclature system uses the prefix *ortho-* (*o-*) for two adjacent substituents, *meta-* (*m-*) for two substituents with one carbon between them, and *para-* (*p-*) for two substituents opposite each other. When benzene is used as a substituent, it is called the **phenyl group**. Examples of some aromatic compounds are shown in Fig. 22.12.

Benzene is the simplest aromatic molecule. More complex aromatic systems can be viewed as consisting of a number of “fused” benzene rings. Some examples are given in Table 22.3.

**FIGURE 22.12**

Some selected substituted benzenes and their names. Common names are given in parentheses.

TABLE 22.3 More Complex Aromatic Systems

Structural Formula	Name	Use of Effect
	Naphthalene	Formerly used in mothballs
	Anthracene	Dyes
	Phenanthrene	Dyes, explosives, and synthesis of drugs
	3,4-Benzpyrene	Active carcinogen found in smoke and smog

22.4 Hydrocarbon Derivatives

The vast majority of organic molecules contain elements in addition to carbon and hydrogen. However, most of these substances can be viewed as **hydrocarbon derivatives**, molecules that are fundamentally hydrocarbons but that have additional atoms or groups of atoms called **functional groups**. The common functional groups

TABLE 22.4 The Common Functional Groups

Class	Functional Group	General Formula*	Example
Halohydrocarbons	—X (F, Cl, Br, I)	R—X	CH ₃ I Iodomethane (methyl iodide)
Alcohols	—OH	R—OH	CH ₃ OH Methanol (methyl alcohol)
Ethers	—O—	R—O—R'	CH ₃ OCH ₃ Dimethyl ether
Aldehydes	$\begin{array}{c} \text{O} \\ \parallel \\ \text{—C—H} \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R—C—H} \end{array}$	CH ₂ O Methanal (formaldehyde)
Ketones	$\begin{array}{c} \text{O} \\ \parallel \\ \text{—C—} \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R—C—R'} \end{array}$	CH ₃ COCH ₃ Propanone (dimethyl ketone or acetone)
Carboxylic acids	$\begin{array}{c} \text{O} \\ \parallel \\ \text{—C—OH} \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R—C—OH} \end{array}$	CH ₃ COOH Ethanoic acid (acetic acid)
Esters	$\begin{array}{c} \text{O} \\ \parallel \\ \text{—C—O—} \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R—C—O—R'} \end{array}$	CH ₃ COOCH ₂ CH ₃ Ethyl acetate
Amines	—NH ₂	R—NH ₂	CH ₃ NH ₂ Aminomethane (methylamine)

* R and R' represent hydrocarbon fragments.

are listed in Table 22.4. Because each functional group exhibits characteristic chemistry, we will consider the groups separately.

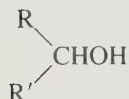
Alcohols

Alcohols are characterized by the presence of the hydroxyl group (—OH). Some common alcohols are shown in Table 22.5. The systematic name for an alcohol is obtained by replacing the final *-e* of the parent hydrocarbon with *-ol*. The position of the —OH group is specified by a number (where necessary) chosen so that it is the smallest of the substituent numbers. Alcohols are classified according to the number of hydrocarbon fragments bonded to the carbon where the —OH group is attached (see margin), where R, R', and R'' (which may be the same or different) represent hydrocarbon fragments.

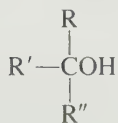
Alcohols usually have much higher boiling points than might be expected from their molar masses. For example, both methanol and ethane have a molar mass of 30, but the boiling point for methanol is 65°C while that for ethane is –89°C. This difference can be understood if we consider the types of intermolecular attractions that occur in these liquids. Ethane molecules are nonpolar and exhibit only weak London dispersion interactions. However, the polar —OH group of methanol produces extensive hydrogen bonding similar to that found in water (see Section 10.1), which results in the relatively high boiling point.



Primary alcohol
(one R group)



Secondary alcohol
(two R groups)



Tertiary alcohol
(three R groups)



A winemaker drawing off a glass of wine in a modern wine cellar.



Ethanol is being tested in selected areas as a fuel for automobiles.

TABLE 22.5 Some Common Alcohols

Formula	Systematic Name	Common Name
CH_3OH	Methanol	Methyl alcohol
$\text{CH}_3\text{CH}_2\text{OH}$	Ethanol	Ethyl alcohol
$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	1-Propanol	<i>n</i> -Propyl alcohol
$\begin{array}{c} \text{CH}_3\text{CHCH}_3 \\ \\ \text{OH} \end{array}$	2-Propanol	Isopropyl alcohol

Although there are many important alcohols, the simplest ones, methanol and ethanol, have the greatest commercial value. Methanol, also known as *wood alcohol* because it was formerly obtained by heating wood in the absence of air, is prepared industrially (approximately 4 million tons annually in the United States) by the hydrogenation of carbon monoxide:



Methanol is used as a starting material for the synthesis of acetic acid and for many types of adhesives, fibers, and plastics. It is also used (and such use may increase) as a motor fuel. Methanol is highly toxic to humans and can lead to blindness and death if ingested.

Ethanol is the alcohol found in beverages such as beer, wine, and whiskey; it is produced by the fermentation of glucose in corn, barley, grapes, and so on:

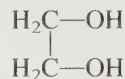


The reaction is catalyzed by the enzymes found in yeast. This reaction can proceed only until the alcohol content reaches about 13% (the percentage found in most wines), at which point the yeast can no longer survive. Beverages with higher alcohol content are made by distilling the fermentation mixture.

Ethanol, like methanol, can be burned in the internal combustion engines of automobiles and is now commonly added to gasoline to form gasohol (see Section 6.6). It is also used in industry as a solvent and for the preparation of acetic acid. The commercial production of ethanol (500,000 tons per year in the United States) is carried out by reaction of water with ethylene:

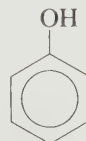


Many polyhydroxyl (more than one —OH group) alcohols are known, the most important being *1,2-ethanediol* (ethylene glycol),



a toxic substance that is the major constituent of most automobile antifreeze solutions.

The simplest aromatic alcohol is

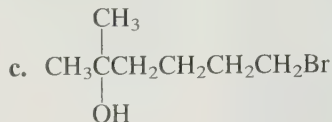
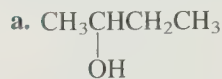


which is commonly called **phenol**. Most of the 1 million tons of phenol produced annually in the United States are used to make polymers for adhesives and plastics.

SAMPLE EXERCISE 22.6

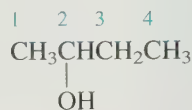
Naming and Classifying Alcohols

For each of the following alcohols, give the systematic name and specify whether the alcohol is primary, secondary, or tertiary.

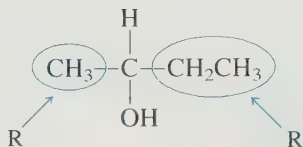


SOLUTION

a. The chain is numbered as follows:



The compound is called 2-butanol, since the —OH group is located at the number 2 position of a four-carbon chain. Note that the carbon to which the —OH is attached also has —CH_3 and $\text{—CH}_2\text{CH}_3$ groups attached:

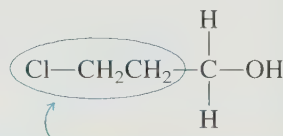


Therefore, this is a *secondary* alcohol.

b. The chain is numbered as follows:

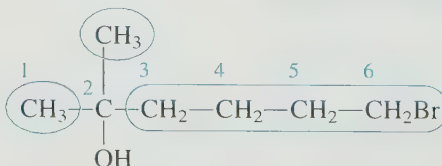


The name is 3-chloro-1-propanol. This is a *primary* alcohol:.



One R group attached to the carbon with the —OH group

c. The chain is numbered as follows:



The name is 6-bromo-2-methyl-2-hexanol. This is a *tertiary* alcohol since the carbon where the —OH is attached also has three other R groups attached.

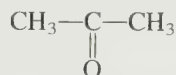
See Exercises 22.55 and 22.56.

Aldehydes and Ketones

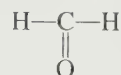
Aldehydes and ketones contain the **carbonyl group**,



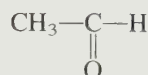
In **ketones** this group is bonded to two carbon atoms, as in acetone,



In **aldehydes** the carbonyl group is bonded to at least one hydrogen atom, as in formaldehyde,



or acetaldehyde,



The systematic name for an aldehyde is obtained from the parent alkane by removing the final *-e* and adding *-al*. For ketones the final *-e* is replaced by *-one*, and a number indicates the position of the carbonyl group where necessary. Examples of common aldehydes and ketones are shown in Fig. 22.13. Note that since the aldehyde functional group always occurs at the end of the carbon chain, the aldehyde carbon is assigned the number 1 when substituent positions are listed in the name.

Ketones often have useful solvent properties (acetone is found in nail polish remover, for example) and are frequently used in industry for this purpose. Aldehydes typically have strong odors. Vanillin is responsible for the pleasant odor in vanilla beans; cinnamaldehyde produces the characteristic odor of cinnamon. On the other hand, the unpleasant odor in rancid butter arises from the presence of butyraldehyde.

Aldehydes and ketones are most often produced commercially by the oxidation of alcohols. For example, oxidation of a *primary* alcohol yields the corresponding aldehyde:

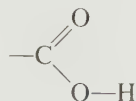


Oxidation of a *secondary* alcohol results in a ketone:

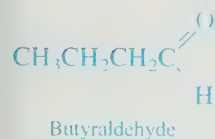
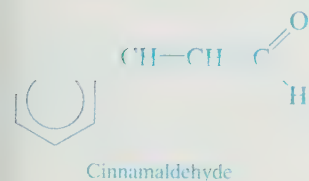
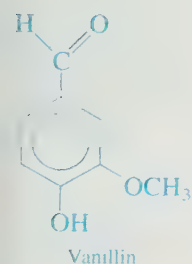


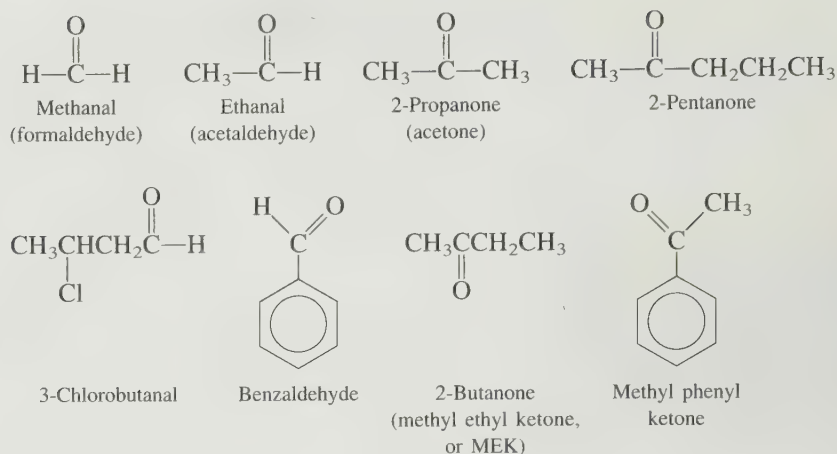
Carboxylic Acids and Esters

Carboxylic acids are characterized by the presence of the **carboxyl group**



Cinnamaldehyde produces the characteristic odor of cinnamon.

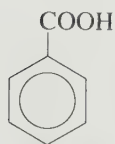


**FIGURE 22.13**

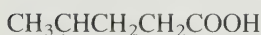
Some common ketones and aldehydes. Note that since the aldehyde functional group always appears at the end of a carbon chain, carbon is assigned the number 1 when the compound is named.



Butanoic acid

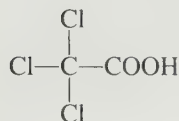


Benzoic acid



Br

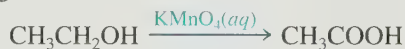
4-Bromopentanoic acid

Trichloroethanoic acid
(trichloroacetic acid)**FIGURE 22.14**

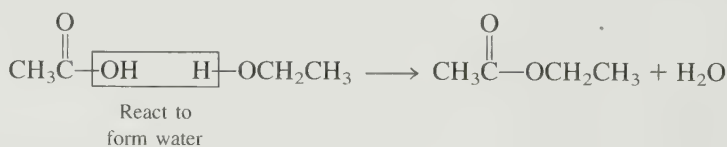
Some carboxylic acids.

that gives an acid of the general formula RCOOH . Typically, these molecules are weak acids in aqueous solution (see Section 14.5). Organic acids are named from the parent alkane by dropping the final *-e* and adding *-oic*. Thus CH_3COOH , commonly called acetic acid, has the systematic name ethanoic acid, since the parent alkane is ethane. Other examples of carboxylic acids are shown in Fig. 22.14.

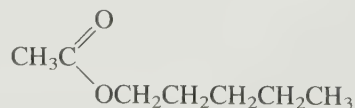
Many carboxylic acids are synthesized by oxidizing primary alcohols with a strong oxidizing agent. For example, ethanol can be oxidized to acetic acid by using potassium permanganate:



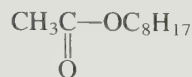
A carboxylic acid reacts with an alcohol to form an **ester** and a water molecule. For example, the reaction of acetic acid with ethanol produces ethyl acetate and water:



Esters often have a sweet, fruity odor that is in contrast to the often pungent odors of the parent carboxylic acids. For example, the odor of bananas is caused by *n*-amyl acetate,



and that of oranges is caused by *n*-octyl acetate,



The systematic name for an ester is formed by changing the *-oic* ending of the parent acid to *-oate*. The parent alcohol chain is named first with a *-yl* ending. For example, the systematic name for *n*-octyl acetate is *n*-octylethanoate (from ethanoic acid).

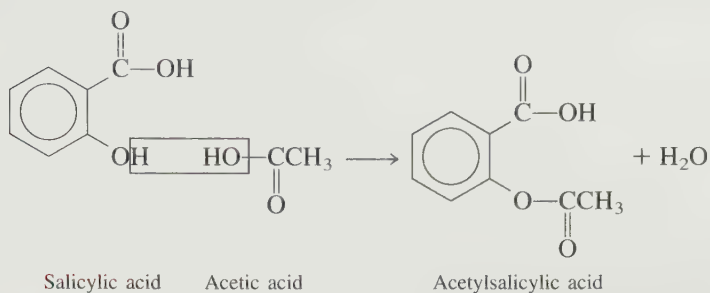


Aspirin tablets.



Computer-generated space-filling model of acetylsalicylic acid (aspirin).

A very important ester is formed from the reaction of salicylic acid and acetic acid:



The product is acetylsalicylic acid, commonly known as *aspirin*, which is used in huge quantities as an analgesic (painkiller).

Amines

Amines are probably best viewed as derivatives of ammonia in which one or more N—H bonds are replaced by N—C bonds. The resulting amines are classified as *primary* if one N—C bond is present, *secondary* if two N—C bonds are present, and *tertiary* if all three N—H bonds in NH_3 have been replaced by N—C bonds (Fig. 22.15). Examples of some common amines are given in Table 22.6.

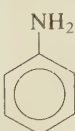
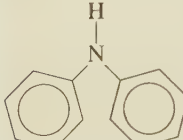
Common names are often used for simple amines; the systematic nomenclature for more complex molecules uses the name *amino-* for the —NH_2 functional group. For example, the molecule



is named 2-aminobutane.

Many amines have unpleasant “fishlike” odors. For example, the odors associated with decaying animal and human tissues are caused by amines such as putrescine ($\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$) and cadaverine ($\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$).

TABLE 22.6 Some Common Amines

Formula	Common Name	Type
CH_3NH_2	Methylamine	Primary
$\text{CH}_3\text{CH}_2\text{NH}_2$	Ethylamine	Primary
$(\text{CH}_3)_2\text{NH}$	Dimethylamine	Secondary
$(\text{CH}_3)_3\text{N}$	Trimethylamine	Tertiary
	Aniline	Primary
	Diphenylamine	Secondary

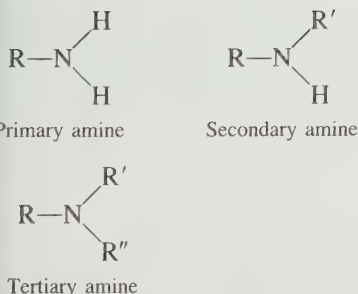


FIGURE 22.15 The general formulas for primary, secondary, and tertiary amines. R, R', and R'' represent carbon-containing substituents.

Aromatic amines are primarily used to make dyes. Since many of them are carcinogenic, they must be handled with great care.

22.5 Polymers



The soybeans on the left are coated with a red acrylic polymer to delay soybean emergence. This allows farmers to plant their crops more efficiently.



A radio from the 1930s made of Bakelite.



Nylon netting magnified 62 times.

Polymers are large, usually chainlike molecules that are built from small molecules called *monomers*. Polymers form the basis for synthetic fibers, rubbers, and plastics and have played a leading role in the revolution that has been brought about in daily life by chemistry. It has been estimated that about 50% of the industrial chemists in the United States work in some area of polymer chemistry, a fact that illustrates just how important polymers are to our economy and standard of living.

The Development and Properties of Polymers

The development of the polymer industry provides a striking example of the importance of serendipity in the progress of science. Many discoveries in polymer chemistry arose from accidental observations that scientists followed up.

The age of plastics might be traced to a day in 1846 when Christian Schoenbein, a chemistry professor at the University of Basel in Switzerland, spilled a flask containing nitric and sulfuric acids. In his hurry to clean up the spill, he grabbed his wife's cotton apron, which he then rinsed out and hung up in front of a hot stove to dry. Instead of drying, the apron flared and burned.

Very interested in this event, Schoenbein repeated the reaction under more controlled conditions and found that the new material, which he correctly concluded to be nitrated cellulose, had some surprising properties. As he had experienced, the nitrated cellulose is extremely flammable and, under certain circumstances, highly explosive. In addition, he found that it could be molded at moderate temperatures to give objects that were, upon cooling, tough but elastic. Predictably, the explosive nature of the substance was initially of more interest than its other properties, and cellulose nitrate rapidly became the basis for smokeless gun powder. Although Schoenbein's discovery cannot be described as a truly synthetic polymer (because he simply found a way to modify the natural polymer cellulose), it formed the basis for a large number of industries that grew up to produce photographic films, artificial fibers, and molded objects of all types.

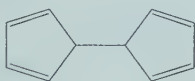
The first synthetic polymers were produced as by-products of various organic reactions and were regarded as unwanted contaminants. Thus the first preparations of many of the polymers now regarded as essential to our modern lifestyle were thrown away in disgust. One chemist who refused to be defeated by the "tarry" products obtained when he reacted phenol with formaldehyde was the Belgian-American chemist Leo H. Baekeland (1863–1944). Baekeland's work resulted in the first completely synthetic plastic (called Bakelite), a substance that when molded to a certain shape under high pressure and temperature cannot be softened again or dissolved. Bakelite is a **thermoset polymer**. In contrast, cellulose nitrate is a **thermoplastic polymer**; that is, it can be remelted after it has been molded.

The discovery of Bakelite in 1907 spawned a large plastics industry, producing telephones, billiard balls, and insulators for electrical devices. During the early days of polymer chemistry, there was a great deal of controversy over the nature of these materials. Although the German chemist Hermann Staudinger speculated in 1920

Heal Thyself

One major problem with structural materials is that they crack and weaken as they age. The human body has mechanisms for healing itself if the skin is cut or a bone is broken. However, inanimate materials have had no such mechanisms—until now. Scientists at the University of Illinois at Urbana–Champaign (UIUC) have invented a plastic that automatically heals microscopic cracks before they can develop into large cracks that would degrade the usefulness of the material. This accomplishment was achieved by an interdisciplinary team of scientists including aeronautical engineering professors Scott White and Philippe Geubelle, applied mechanics professor Nancy Sottos, and chemistry professor Jeffrey Moore.

The self-healing system is based on microcapsules containing liquid dicyclopentadiene



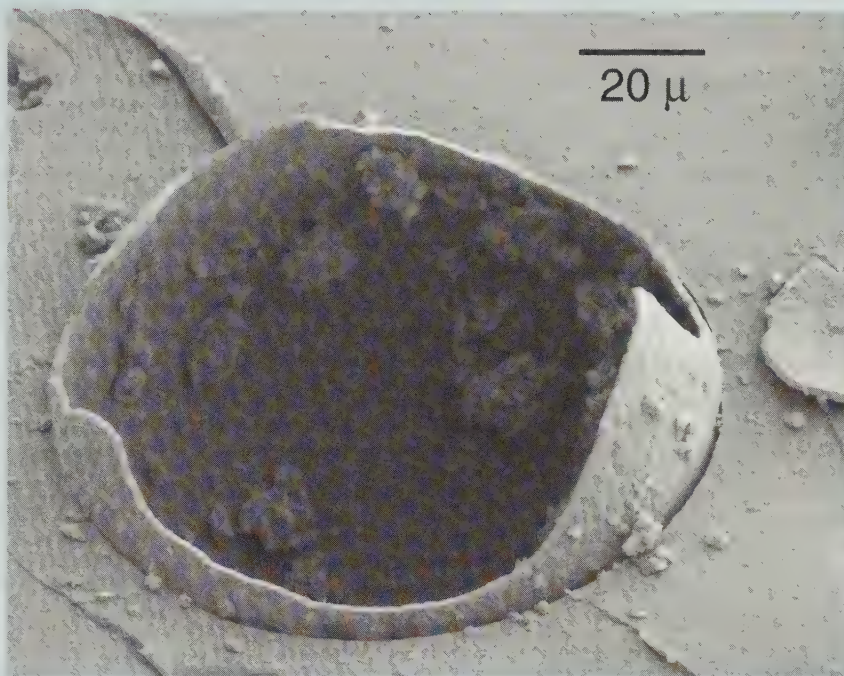
Dicyclopentadiene

that are blended into the plastic. When a microscopic crack develops, it encounters and breaks a microcapsule. The dicyclopentadiene then leaks out, where it encounters a catalyst (blended into the plastic when it was formulated) that mediates a repair polymerization process. This process involves opening the cyclopentadiene rings, which leads to a highly cross-linked repair of the crack.

The trickiest part of the repair mechanism is to get the microcapsules to be the correct size and to have the appropriate wall strength. They must be small enough not to degrade the strength of the plastic. The walls must also

be thick enough to survive the molding of the plastic but thin enough to burst as the lengthening crack reaches them.

Self-healing materials should have many applications. The U.S. Air Force, which partially funded the research at UIUC, is interested in using the materials in tanks that hold gases and liquids under pressure. The current materials used for these tanks are subject to microcracks that eventually grow, causing the tanks to leak. Self-healing materials would also be valuable in situations where repair is impossible or impractical, such as electronic circuit boards, components of deep space probes, and implanted medical devices.



A scanning electron microscope image showing the fractured plane of a self-healing material with a ruptured microcapsule in a thermosetting matrix.

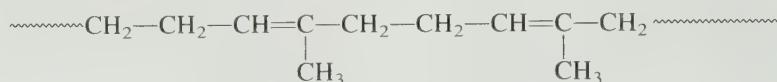
that polymers were very large molecules held together by strong chemical bonds, most chemists of the time assumed that these materials were much like colloids, in which small molecules are aggregated into large units by forces weaker than chemical bonds.

One chemist who contributed greatly to the understanding of polymers as giant molecules was Wallace H. Carothers of the DuPont Chemical Company. Among his accomplishments was the preparation of nylon. The nylon story further illustrates the importance of serendipity in scientific research. When nylon is first prepared, the resulting product is a sticky material with little structural integrity. Because of

this, it was initially put aside as having no apparently useful characteristics. However, Julian Hill, a chemist in the Carothers research group, one day put a small ball of this nylon on the end of a stirring rod and drew it away from the remaining sticky mass, forming a string. He noticed the silky appearance and strength of this thread and realized that nylon could be drawn into useful fibers.

The reason for this behavior of nylon is now understood. When nylon is first formed, the individual polymer chains are oriented randomly, like cooked spaghetti, and the substance is highly amorphous. However, when drawn out into a thread, the chains tend to line up (the nylon becomes more crystalline), which leads to increased hydrogen bonding between adjacent chains. This increase in crystallinity, along with the resulting increase in hydrogen-bonding interactions, leads to strong fibers and thus to a highly useful material. Commercially, nylon is produced by forcing the raw material through a *spinneret*, a plate containing small holes, which forces the polymer chains to line up.

Another property that adds strength to polymers is **crosslinking**, the existence of covalent bonds between adjacent chains. The structure of Bakelite is highly crosslinked, which accounts for the strength and toughness of this polymer. Another example of crosslinking occurs in the manufacture of rubber. Raw natural rubber consists of chains of the type

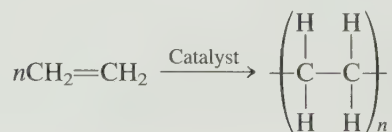


and is a soft, sticky material unsuitable for tires. However, in 1839 Charles Goodyear (1800–1860), an American chemist, accidentally found that if sulfur is added to rubber and the resulting mixture is heated (a process called **vulcanization**), the resulting rubber is still elastic (reversibly stretchable) but is much stronger. This change in character occurs because sulfur atoms become bonded between carbon atoms on different chains. These sulfur atoms form bridges between the polymer chains, thus linking the chains together.

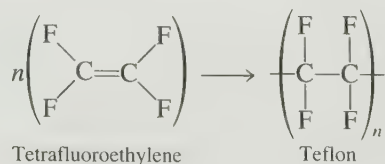
Charles Goodyear tried for many years to change natural rubber into a useful product. In 1839 he accidentally dropped some rubber containing sulfur on a hot stove. Noting that the rubber did not melt as expected, Goodyear pursued this lead and developed vulcanization.

Types of Polymers

The simplest and one of the best-known polymers is *polyethylene*, which is constructed from ethylene monomers:



where n represents a large number (usually several thousand). Polyethylene is a tough, flexible plastic used for piping, bottles, electrical insulation, packaging films, garbage bags, and many other purposes. Its properties can be varied by using substituted ethylene monomers. For example, when tetrafluoroethylene is the monomer, the polymer Teflon is obtained:

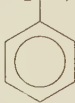


Cross-linking gives the rubber in these tires strength and toughness.

The discovery of Teflon, a very important substituted polyethylene, is another illustration of the role of chance in chemical research. In 1938 a DuPont chemist named Roy Plunkett was studying the chemistry of gaseous tetrafluoroethylene. He synthesized about 100 pounds of the chemical and stored it in steel cylinders. When one of the cylinders failed to produce perfluoroethylene gas when the valve was opened, the cylinder was cut open to reveal a white powder. This powder turned out to be a polymer of perfluoroethylene, which was eventually developed into Teflon. Because of the resistance of the strong C—F bonds to chemical attack, Teflon is an inert, tough, and nonflammable material widely used for electrical insulation, non-stick coatings on cooking utensils, and bearings for low-temperature applications.

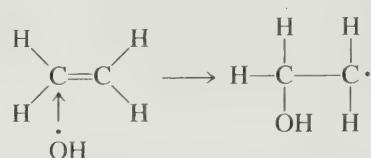
Other polyethylene-type polymers are made from monomers containing chloro, methyl, cyano, and phenyl substituents, as summarized in Table 22.7. In each case

TABLE 22.7 Some Common Synthetic Polymers, Their Monomers and Applications

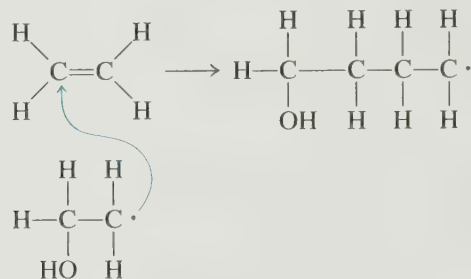
Monomer		Polymer		
Name	Formula	Name	Formula	Uses
Ethylene	$\text{H}_2\text{C}=\text{CH}_2$	Polyethylene	$-(\text{CH}_2-\text{CH}_2)_n-$	Plastic piping, bottles, electrical insulation, toys
Propylene	$\begin{array}{c} \text{H} \\ \\ \text{H}_2\text{C}=\text{C} \\ \\ \text{CH}_3 \end{array}$	Polypropylene	$-(\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2)_n-$	Film for packaging, carpets, lab wares, toys
Vinyl chloride	$\begin{array}{c} \text{H} \\ \\ \text{H}_2\text{C}=\text{C} \\ \\ \text{Cl} \end{array}$	Polyvinyl chloride (PVC)	$-(\text{CH}_2-\underset{\text{Cl}}{\text{CH}})_n-$	Piping, siding, floor tile, clothing, toys
Acrylonitrile	$\begin{array}{c} \text{H} \\ \\ \text{H}_2\text{C}=\text{C} \\ \\ \text{CN} \end{array}$	Polyacrylonitrile (PAN)	$-(\text{CH}_2-\underset{\text{CN}}{\text{CH}})_n-$	Carpets, fabrics
Tetrafluoroethylene	$\text{F}_2\text{C}=\text{CF}_2$	Teflon	$-(\text{CH}_2-\text{CH}_2)_n-$	Cooking utensils, electrical insulation, bearings
Styrene	$\begin{array}{c} \text{H} \\ \\ \text{H}_2\text{C}=\text{C} \\ \\ \text{C}_6\text{H}_5 \end{array}$	Polystyrene	$-(\text{CH}_2\text{CH})_n-$ 	Containers, thermal insulation, toys
Butadiene	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H}_2\text{C}=\text{C}-\text{C}=\text{CH}_2 \end{array}$	Polybutadiene	$-(\text{CH}_2\text{CH}=\text{CHCH}_2)_n-$	Tire tread, coating resin
Butadiene and styrene	(See above.)	Styrene-butadiene rubber	$-(\underset{\text{C}_6\text{H}_5}{\text{CH}}-\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2)_n-$ 	Synthetic rubber

the double carbon–carbon bond in the substituted ethylene monomer becomes a single bond in the polymer. The different substituents lead to a wide variety of properties.

The polyethylene polymers illustrate one of the major types of polymerization reactions, called **addition polymerization**, in which the monomers simply “add together” to produce the polymer. No other products are formed. The polymerization process is initiated by a **free radical** (a species with an unpaired electron) such as the hydroxyl radical ($\text{HO}\cdot$). The free radical attacks and breaks the π bond of an ethylene molecule to form a new free radical,

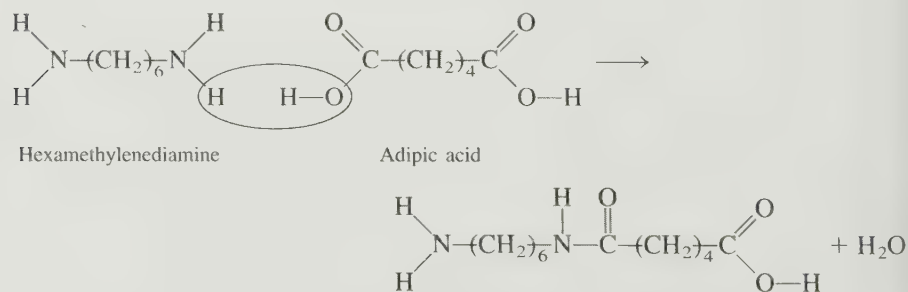


which is then available to attack another ethylene molecule:

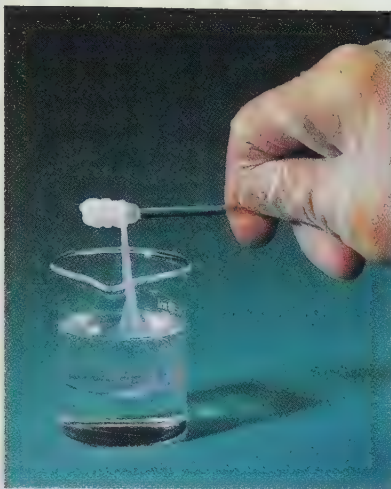


Repetition of this process thousands of times creates a long-chain polymer. Termination of the growth of the chain occurs when *two radicals* react to form a bond, a process that consumes two radicals without producing any others.

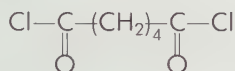
Another common type of polymerization is **condensation polymerization**, in which a small molecule, such as water, is formed for each extension of the polymer chain. The most familiar polymer produced by condensation is *nylon*. Nylon is a **copolymer**, since two different types of monomers combine to form the chain; a **homopolymer** is the result of polymerizing a single type of monomer. One common form of nylon is produced when hexamethylenediamine and adipic acid react by splitting out a water molecule to form a C—N bond:



The molecule formed, called a **dimer** (two monomers joined), can undergo further condensation reactions since it has an amino group at one end and a carboxyl group

**FIGURE 22.16**

The reaction to form nylon can be carried out at the interface of two immiscible liquid layers in a beaker. The bottom layer contains adipoyl chloride,

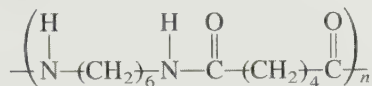


dissolved in CCl_4 , and the top layer contains hexamethylenediamine,



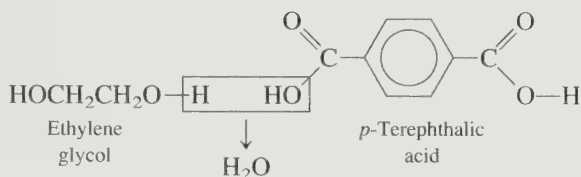
dissolved in water. A molecule of HCl is formed as each $\text{C}-\text{N}$ bond forms.

at the other. Thus both ends are free to react with another monomer. Repetition of this process leads to a long chain of the type

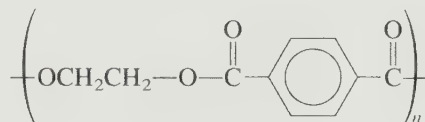


which is the basic structure of nylon. The reaction to form nylon occurs quite readily and is often used as a lecture demonstration (see Fig. 22.16). The properties of nylon can be varied by changing the number of carbon atoms in the chain of the acid or amine monomer.

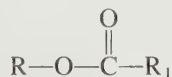
More than 1 million tons of nylon are produced annually in the United States for use in clothing, carpets, rope, and so on. Many other types of condensation polymers are also produced. For example, Dacron is a copolymer formed from the condensation reaction of ethylene glycol (a dialcohol) and *p*-terephthalic acid (a dicarboxylic acid):



The repeating unit of Dacron is



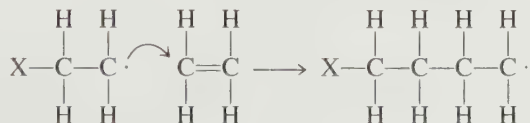
Note that this polymerization involves a carboxylic acid and an alcohol forming an ester group:



Thus Dacron is called a **polyester**. By itself or blended with cotton, Dacron is widely used in fibers for the manufacture of clothing.

Polymers Based on Ethylene

A large section of the polymer industry involves the production of macromolecules from ethylene or substituted ethylenes. As discussed previously, ethylene molecules polymerize by addition after the double bond has been broken by some initiator:



This process continues by adding new ethylene molecules to eventually give polyethylene, a thermoplastic material.

There are two forms of polyethylene: low-density polyethylene (LDPE) and high-density polyethylene (HDPE). The chains in LDPE contain many branches and

CHEMICAL IMPACT

Wallace Hume Carothers

Wallace H. Carothers, a brilliant organic chemist who was principally responsible for the development of nylon and the first synthetic rubber (Neoprene), was born in 1896 in Burlington, Iowa. As a youth, Carothers was fascinated by tools and mechanical devices and spent many hours experimenting. In 1915 he entered Tarkio College in Missouri. Carothers so excelled in chemistry that even before his graduation, he was made a chemistry instructor.

Carothers eventually moved to the University of Illinois at Urbana-Champaign, where he was appointed to the faculty when he completed his Ph.D. in organic chemistry in 1924. He moved to Harvard University in 1926, and then to DuPont in 1928 to participate in a new program in fundamental research. At DuPont, Carothers headed the organic chemistry division, and during his ten years there played a prominent role in laying the foundations of polymer chemistry.

By the age of 33, Carothers had become a world-famous chemist whose advice was sought by almost everyone working in polymers. He was the first industrial chemist to be elected to the prestigious National Academy of Sciences.

Carothers was an avid reader of poetry and a lover of classical music. Unfortunately, he also suffered from severe bouts of depression that finally led to his suicide in 1937 in a Philadelphia hotel room, where he drank a cyanide solution. He was 41 years old. Despite the brevity of his career,



Wallace H. Carothers.

Carothers was truly one of the finest American chemists of all time. His great intellect, his love of chemistry, and his insistence on perfection produced his special genius.

psi is the abbreviation for pounds per square inch: 15 psi $\approx$ 1 atm.

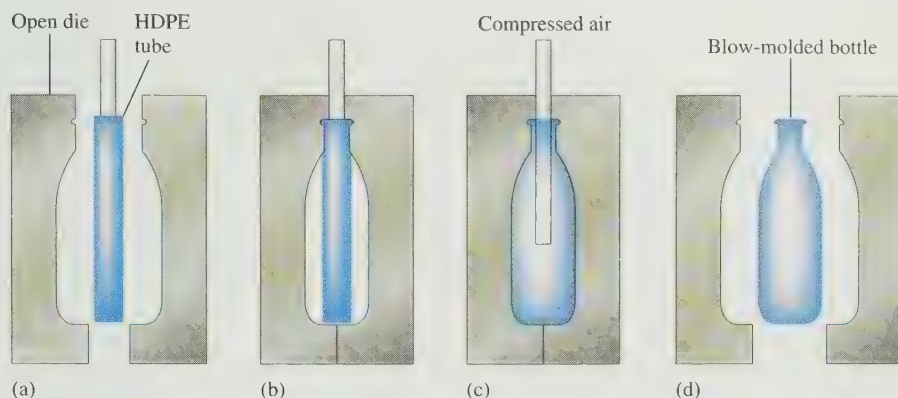
thus do not pack as tightly as those in HDPE, which consist of mostly straight-chain molecules.

Traditionally, LDPE has been manufactured under conditions of high pressure ($\approx 20,000$ psi) and high temperature (500°C). These severe reaction conditions require specially designed equipment, and for safety reasons the reaction usually has been run behind a reinforced concrete barrier. More recently, lower reaction pressures and temperatures have become possible through the use of catalysts. One catalytic system using triethylaluminum, $\text{Al}(\text{C}_2\text{H}_5)_3$, and titanium(IV) chloride was developed by Karl Ziegler in Germany and Giulio Natta in Italy. Although this catalyst is very efficient, it catches fire on contact with air and must be handled very carefully. A safer catalytic system was developed at Phillips Petroleum Company. It uses a chromium(III) oxide (Cr_2O_3) and aluminosilicate catalyst and has mainly taken over in the United States. The product of the catalyzed reaction is highly linear (unbranched) and is often called *linear low-density polyethylene*. It is very similar to HDPE.

The major use of LDPE is in the manufacture of the tough transparent film that is used in packaging so many consumer goods. Two-thirds of the approximately 10 billion pounds of LDPE produced annually in the United States are used for this purpose. The major use of HDPE is for blow-molded products, such as bottles for consumer products (see Fig. 22.17).

FIGURE 22.17

A major use of HDPE is for blow-molded objects such as bottles for soft drinks, shampoos, bleaches, and so on. (a) A tube composed of HDPE is inserted into the mold (die). (b) The die closes, sealing the bottom of the tube. (c) Compressed air is forced into the warm HDPE tube, which then expands to take the shape of the die. (d) The molded bottle is removed from the die.



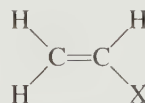
Molecular weight (not molar mass) is the common terminology in the polymer industry.

The useful properties of polyethylene are due primarily to its high molecular weight (molar mass). Although the strengths of the interactions between specific points on the nonpolar chains are quite small, the chains are so long that these small attractions accumulate to a very significant value, so that the chains stick together very tenaciously. There is also a great deal of physical tangling of the lengthy chains. The combination of these interactions gives the polymer strength and toughness. However, a material like polyethylene can be melted and formed into a new shape (thermoplastic behavior), because in the melted state the molecules can readily flow past one another.

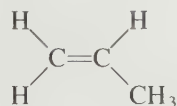
Since a high molecular weight gives a polymer useful properties, one might think that the goal would be to produce polymers with chains as long as possible. However, this is not the case—polymers become much more difficult to process as the molecular weights increase. Most industrial operations require that the polymer flow through pipes as it is processed. But as the chain lengths increase, viscosity also increases. In practice, the upper limit of a polymer's molecular weight is set by the flow requirements of the manufacturing process. Thus the final product often reflects a compromise between the optimal properties for the application and those needed for ease of processing.

Although many polymer properties are greatly influenced by molecular weight, some other important properties are not. For example, chain length does not affect a polymer's resistance to chemical attack. Physical properties such as color, refractive index, hardness, density, and electrical conductivity are also not greatly influenced by molecular weight.

We have already seen that one way of altering the strength of a polymeric materials is to vary the chain length. Another method for modifying polymer behavior involves varying the substituents. For example, if we use a monomer of the type

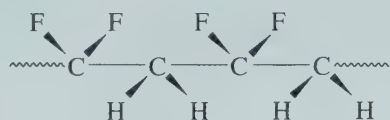


the properties of the resulting polymer depend on the identity of X. The simplest example is polypropylene, whose monomer is



Plastic That Talks and Listens

Imagine a plastic so “smart” that it can be used to sense a baby’s breath, measure the force of a karate punch, sense the presence of a person 100 feet away, or make a balloon that sings. There is a plastic film capable of doing all these things. It’s called polyvinylidene difluoride (PVDF), which has the structure



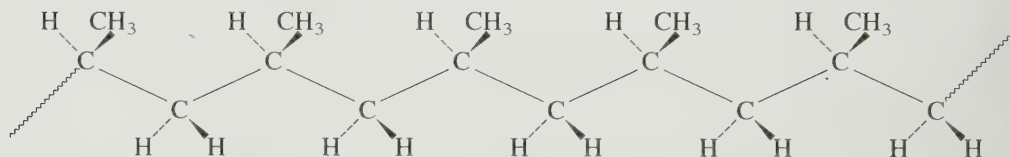
When this polymer is processed in a particular way, it becomes piezoelectric and pyroelectric. A piezoelectric substance produces an electric current when it is physically deformed or alternatively undergoes a deformation caused by the application of a current. A pyroelectric material is one that develops an electrical potential in response to a change in its temperature.

Because PVDF is piezoelectric, it can be used to construct a paper-thin microphone; it responds to sound by producing a current proportional to the deformation caused by the sound waves. A ribbon of PVDF plastic one-quarter of

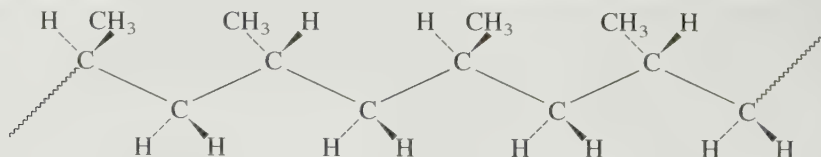
an inch wide could be strung along a hallway and used to listen to all the conversations going on as people walk through. On the other hand, electric pulses can be applied to the PVDF film to produce a speaker. A strip of PVDF film glued to the inside of a balloon can play any song stored on a microchip attached to the film—hence a balloon that can sing, “Happy Birthday”, at a party. The PVDF film can also be used to construct a sleep apnea monitor, which, when placed beside the mouth of a sleeping infant, will set off an alarm if the breathing stops, thus helping to prevent sudden infant death syndrome (SIDS). The same type of film is used by the U.S. Olympic karate team to measure the force of kicks and punches as the team trains. Also, gluing two strips of film together gives a material that curls in response to a current, creating an artificial muscle. In addition, because the PVDF film is pyroelectric, it responds to the infrared (heat) radiation emitted by a human as far away as 100 feet, making it useful for burglar alarm systems.

Making the PVDF polymer piezoelectric and pyroelectric requires some very special processing, which makes it costly (\$10 per square foot). This expense seems a small price to pay for its near-magical properties.

and that has the form



The CH_3 groups can be arranged on the same side of the chain (called an **isotactic chain**) as shown above, can alternate (called a **syndiotactic chain**) as shown below,

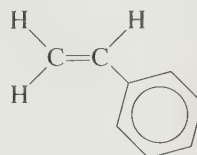


or can be randomly distributed (called an **atactic chain**).

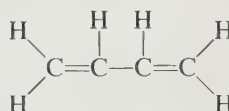
The chain arrangement has a significant effect on the polymer’s properties. Most polypropylene is made using the Ziegler-Natta catalyst, $\text{Al}(\text{C}_2\text{H}_5)_3 \cdot \text{TiCl}_4$, which produces highly isotactic chains that pack together quite closely. As a result, polypropylene is more crystalline, and therefore stronger and harder, than polyethylene. The major uses of polypropylene are for molded parts (40%), fibers (35%), and packaging films (10%). Polypropylene fibers are especially useful for athletic

wear because they do not absorb water from perspiration, as cotton does. Rather, the moisture is drawn away from the skin to the surface of the polypropylene garment, where it can evaporate. The annual U.S. production of polypropylene is about 7 billion pounds.

Another related polymer, **polystyrene**, is constructed from the monomer styrene,



Pure polystyrene is too brittle for many uses, so most polystyrene-based polymers are actually *copolymers* of styrene and butadiene,

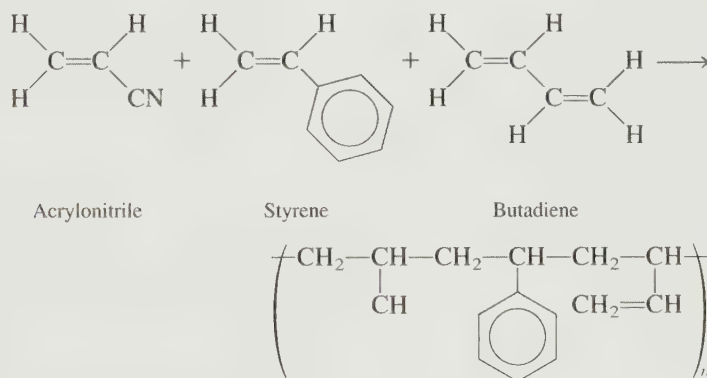


thus incorporating bits of butadiene rubber into the polystyrene matrix. The resulting polymer is very tough and is often used as a substitute for wood in furniture.

Another polystyrene-based product is acrylonitrile-butadiene-styrene (ABS), a tough, hard, and chemically resistant plastic used for pipes and for items such as radio housings, telephone cases, and golf club heads, for which shock resistance is an essential property. Originally, ABS was produced by copolymerization of the three monomers:

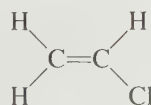


PVC pipe is widely used in industry.



It is now prepared by a special process called *grafting*, in which butadiene is polymerized first, and then the cyanide and phenyl substituents are added chemically.

Another high-volume polymer, **polyvinyl chloride (PVC)**, is constructed from the monomer vinyl chloride,

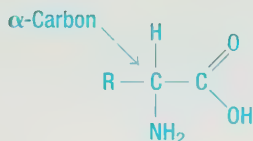


22.6 Natural Polymers

Proteins



The protein in muscles enables them to contract.



At the pH in biological fluids, the amino acids shown in Fig. 22.18 exist in a different form, with the proton of the —COOH group transferred to the —NH_2 group. For example, glycine would be in the form $\text{H}_3^+\text{NCH}_2\text{COO}^-$.

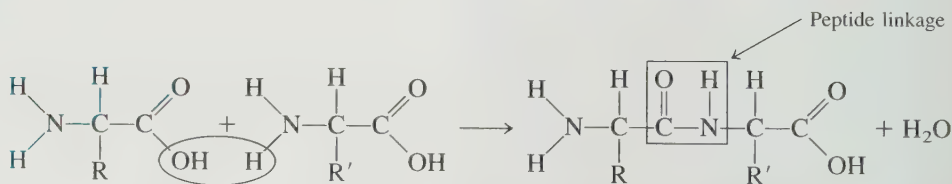
We have seen that many useful synthetic materials are polymers. Thus it should not be surprising that a great many natural materials are also polymers: starch, hair, silicate chains in soil and rocks, silk and cotton fibers, and the cellulose in woody plants, to name only a few.

In this section we consider a class of natural polymers, the **proteins**, which make up about 15% of our bodies and have molecular weights (molar masses) that range from about 6000 to over 1,000,000 grams per mole. Proteins perform many functions in the human body. **Fibrous proteins** provide structural integrity and strength for many types of tissue and are the main components of muscle, hair, and cartilage. Other proteins, usually called **globular proteins** because of their roughly spherical shape, are the “worker” molecules of the body. These proteins transport and store oxygen and nutrients, act as catalysts for the thousands of reactions that make life possible, fight invasion by foreign objects, participate in the body’s many regulatory systems, and transport electrons in the complex process of metabolizing nutrients.

The building blocks of all proteins are the α -amino acids, where R may represent H, CH_3 , or a more complex substituent. These molecules are called α -amino acids because the amino group (—NH_2) is always attached to the α -carbon, the one next to the carboxyl group ($\text{—CO}_2\text{H}$). The 20 amino acids most commonly found in proteins are shown in Fig. 22.18.

Note from Fig. 22.18 that the amino acids are grouped into polar and nonpolar classes, determined by the R groups, or **side chains**. Nonpolar side chains contain mostly carbon and hydrogen atoms, whereas polar side chains contain large numbers of nitrogen and oxygen atoms. This difference is important, because polar side chains are *hydrophilic* (water-loving), but nonpolar side chains are *hydrophobic* (water-fearing), and this characteristic greatly affects the three-dimensional structure of the resulting protein.

The protein polymer is built by condensation reactions between amino acids. For example,



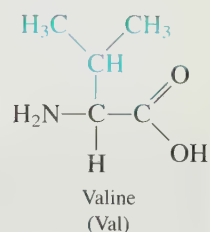
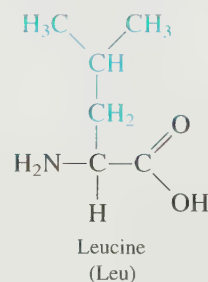
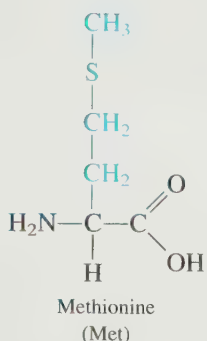
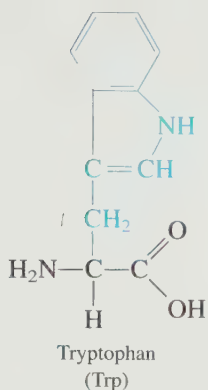
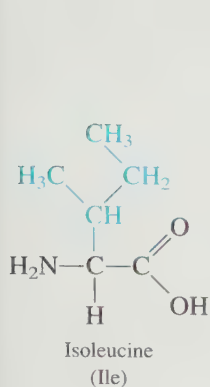
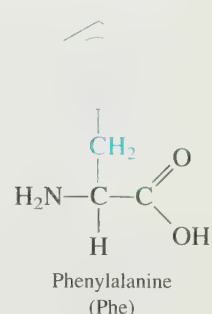
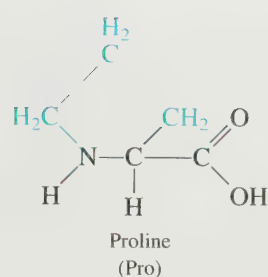
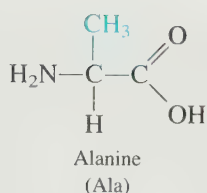
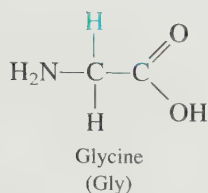
The product shown above is called a **dipeptide**. This name is used because the structure



The peptide linkage is also found in nylon (see Section 22.5).

is called a **peptide linkage** by biochemists. (The same grouping is called an amide by organic chemists.) Additional condensation reactions lengthen the chain to produce a **polypeptide**, eventually yielding a protein.

Nonpolar R groups



Polar R groups

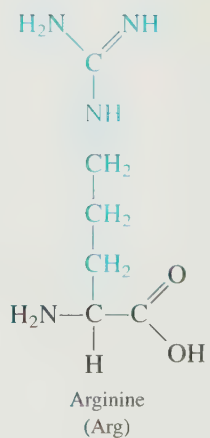
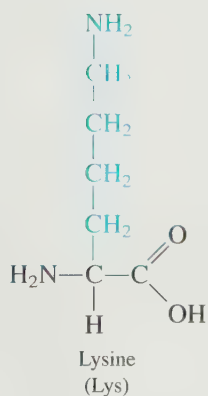
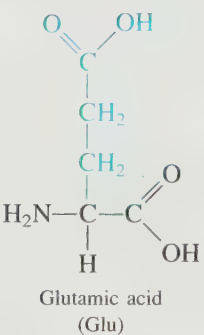
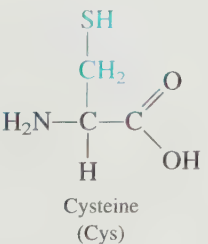
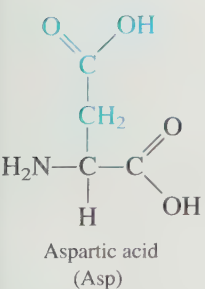
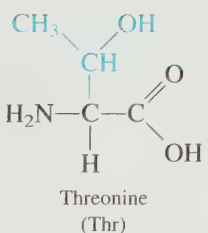
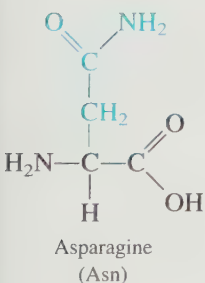
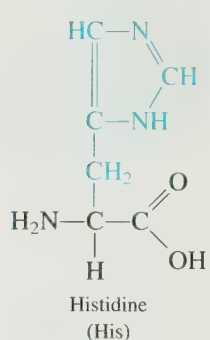
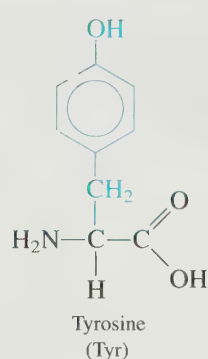
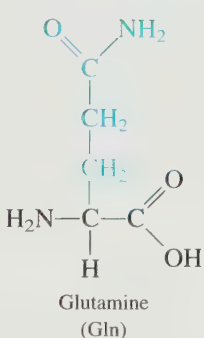
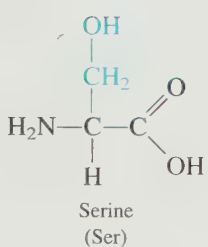
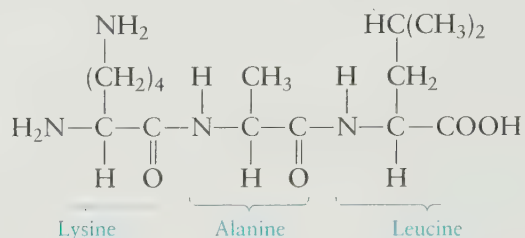


FIGURE 22.18

The 20 α -amino acids found in most proteins. The R group is shown in color.

You can imagine that with 20 amino acids, which can be assembled in any order, there is essentially an infinite variety possible in the construction of proteins. This flexibility allows an organism to tailor proteins for the many types of functions that must be carried out.

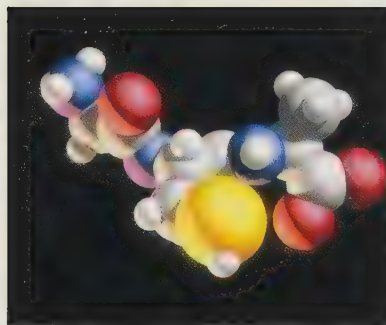
The order, or sequence, of amino acids in the protein chain is called the **primary structure**, conveniently indicated by using three-letter codes for the amino acids (see Fig. 22.18), where it is understood that the terminal carboxyl group is on the right and the terminal amino group is on the left. For example, one possible sequence for a tripeptide containing the amino acids lysine, alanine, and leucine is



which is represented in the shorthand notation by

lys-ala-leu

Note from Sample Exercise 22.7 that there are six sequences possible for a polypeptide with three given amino acids. There are three possibilities for the first amino acid (any one of the three given amino acids), there are two possibilities for the second amino acid (one has already been accounted for), but there is only one possibility left for the third amino acid. Thus the number of sequences is $3 \times 2 \times 1 = 6$. The product $3 \times 2 \times 1$ is often written $3!$ (and is called 3 factorial). Similar reasoning shows that for a polypeptide with four amino acids, there are $4!$, or $4 \times 3 \times 2 \times 1 = 24$, possible sequences.



A tripeptide containing glycine, cysteine, and alanine.

SAMPLE EXERCISE 22.7

Tripeptide Sequences

Write the sequences of all possible tripeptides composed of the amino acids tyrosine, histidine, and cysteine.

SOLUTION

There are six possible sequences:

tyr-his-cys	his-tyr-cys	cys-tyr-his
tyr-cys-his	his-cys-tyr	cys-his-tyr

See Exercise 22.89.

SAMPLE EXERCISE 22.8

Polypeptide Sequences

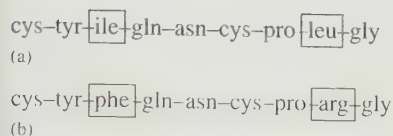
What number of possible sequences exists for a polypeptide composed of 20 different amino acids?

SOLUTION

The answer is $20!$, or

$$20 \times 19 \times 18 \times 17 \times 16 \times \dots \times 5 \times 4 \times 3 \times 2 \times 1 = 2.43 \times 10^{18}$$

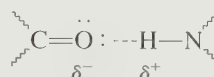
See Exercise 22.90.

**FIGURE 22.19**

The amino acid sequences in (a) oxytocin and (b) vasopressin. The differing amino acids are boxed.

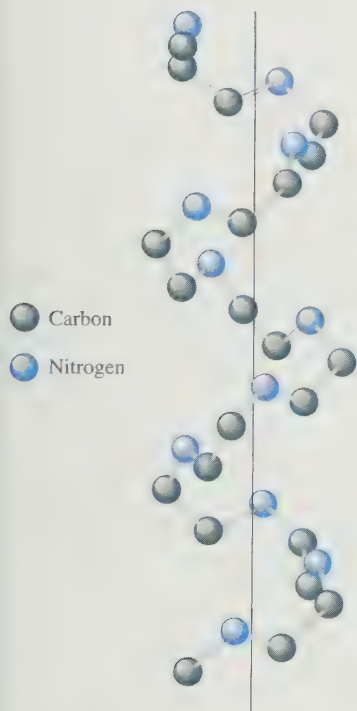
A striking example of the importance of the primary structure of polypeptides can be seen in the differences between *oxytocin* and *vasopressin*. Both of these molecules are nine-unit polypeptides that differ by only two amino acids (Fig. 22.19), yet they perform completely different functions in the human body. Oxytocin is a hormone that triggers contraction of the uterus and milk secretion. Vasopressin raises blood pressure levels and regulates kidney function.

A second level of structure in proteins, beyond the sequence of amino acids, is the arrangement of the chain of the long molecule. The **secondary structure** is determined to a large extent by hydrogen bonding between lone pairs on an oxygen atom in the carbonyl group of an amino acid and a hydrogen atom attached to a nitrogen of another amino acid:

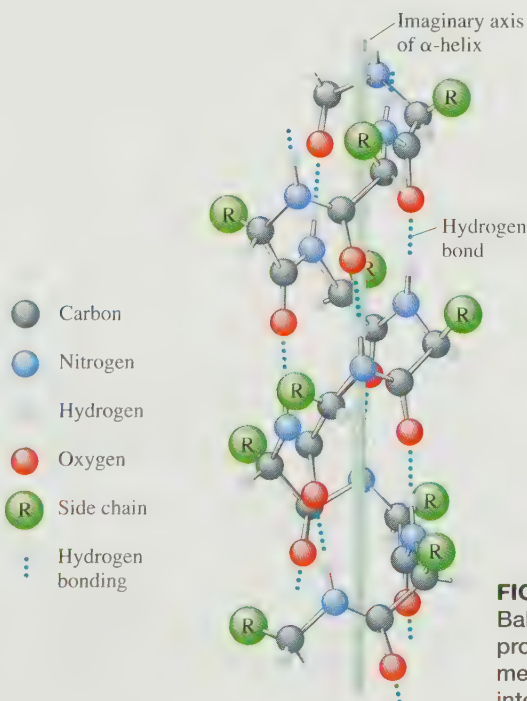


Such interactions can occur *within* the chain coils to form a spiral structure called an **α -helix**, as shown in Fig. 22.20 and Fig. 22.21. This type of secondary structure gives the protein elasticity (springiness) and is found in the fibrous proteins in wool, hair, and tendons. Hydrogen bonding can also occur *between different* protein chains, joining them together in an arrangement called a **pleated sheet**, as shown in Fig. 22.22. Silk contains this arrangement of proteins, making its fibers flexible yet very strong and resistant to stretching. The pleated sheet is also found to muscle fibers. The hydrogen bonds in the α -helical protein are called *intrachain* (within a given protein chain), and those in the pleated sheet are said to be *interchain* (between protein chains).

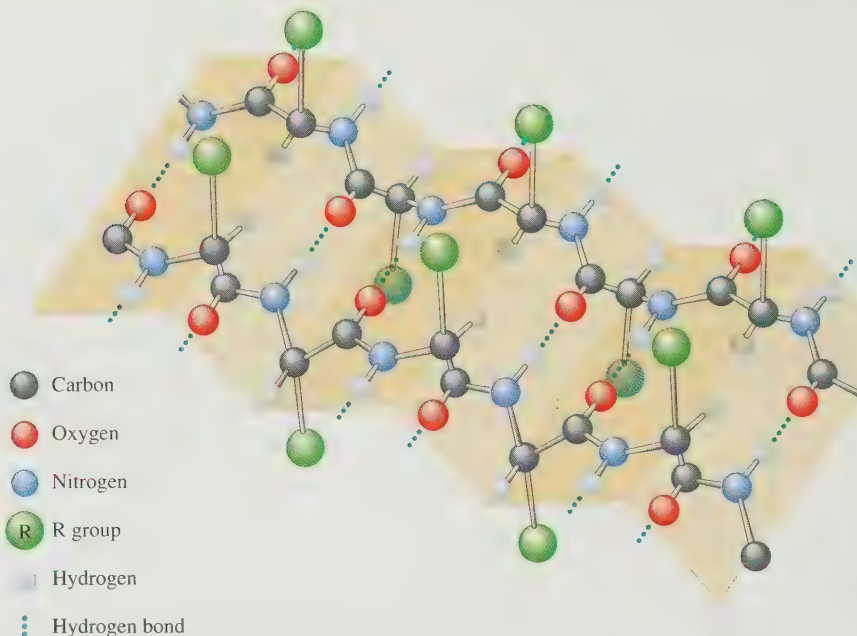
As you might imagine, a molecule as large as a protein has a great deal of flexibility and can assume a variety of overall shapes. The specific shape that a protein

**FIGURE 22.20**

Hydrogen bonding within a protein chain causes it to form a stable helical structure called the α -helix. Only the main atoms in the helical backbone are shown here. The hydrogen bonds are not shown.

**FIGURE 22.21**

Ball-and-stick model of a portion of a protein chain in the α -helical arrangement, showing the hydrogen-bonding interactions.

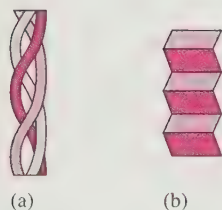
**FIGURE 22.22**

When hydrogen bonding occurs between protein chains rather than within them, a stable structure (the pleated sheet) results. This structure contains many protein chains and is found in natural fibers, such as silk, and in muscles.

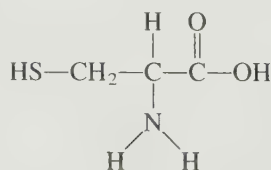
assumes depends on its function. For long, thin structures, such as hair, wool and silk fibers, and tendons, an elongated shape is required. This may involve an α -helical secondary structure, as found in the protein α -keratin in hair and wool or in the collagen found in tendons [Fig. 22.23(a)], or it may involve a pleated-sheet secondary structure, as found in silk [Fig. 22.23(b)]. Many of the proteins in the body having nonstructural functions are globular, such as myoglobin (see Fig. 21.31). Note that the secondary structure of myoglobin is basically α -helical. However, in the areas where the chain bends to give the protein its compact globular structure, the α -helix breaks down to give a secondary configuration known as the **random-coil arrangement**.

The overall shape of the protein, long and narrow or globular, is called its **tertiary structure** and is maintained by several different types of interactions: hydrogen bonding, dipole-dipole interactions, ionic bonds, covalent bonds, and London dispersion forces between nonpolar groups. These bonds, which represent all the bonding types discussed in this text, are summarized in Fig. 22.24.

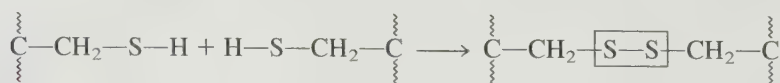
The amino acid *cysteine*

**FIGURE 22.23**

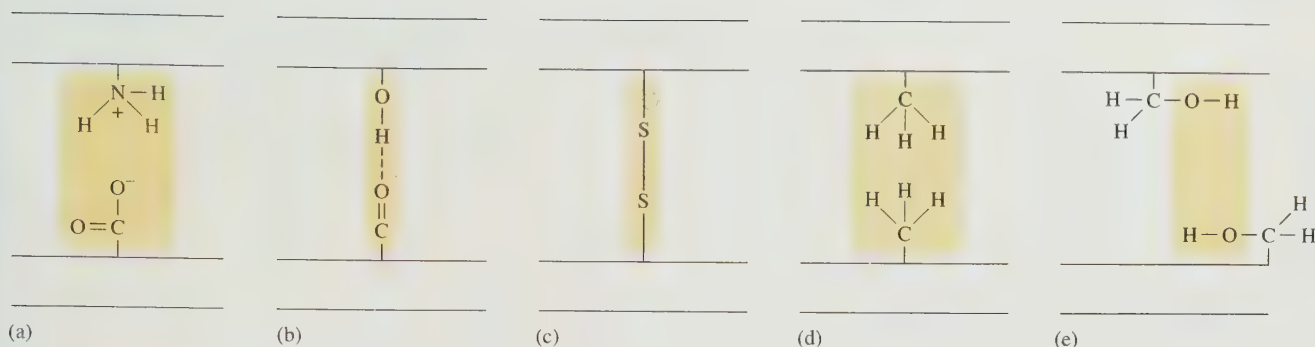
(a) Collagen, a protein found in tendons, consists of three protein chains (each with a helical structure) twisted together to form a superhelix. The result is a long, relatively narrow protein. (b) The pleated-sheet arrangement of many proteins bound together to form the elongated protein found in silk fibers.



plays a special role in stabilizing the tertiary structure of many proteins because the —SH groups on two cysteines can react in the presence of an oxidizing agent to form a S—S bond called a **disulfide linkage**:



A practical application of the chemistry of disulfide bonds is permanent waving of hair, as summarized in Fig. 22.25. The S—S linkages in the protein of hair are broken by treatment with a reducing agent. The hair is then set in curlers to change the

**FIGURE 22.24**

Summary of the various types of interactions that stabilize the tertiary structure of a protein: (a) ionic, (b) hydrogen bonding, (c) covalent, (d) London dispersion, and (e) dipole-dipole.

tertiary protein structure to the desired shape. Then treatment with an oxidizing agent causes new S—S bonds to form, which allow the hair protein to retain the new structure.

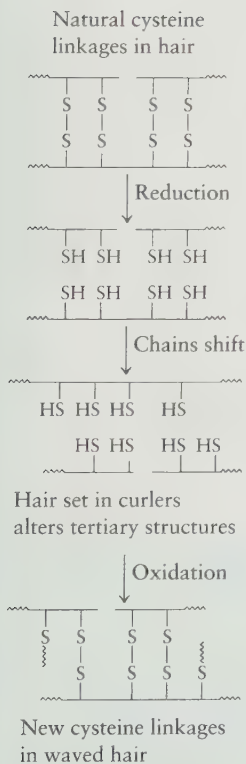
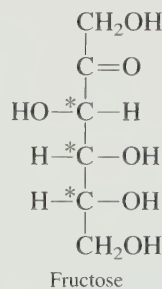
The three-dimensional structure of a protein is crucial to its function. The process of breaking down this structure is called **denaturation** (Fig. 22.26 on page 1081). For example, the denaturation of egg proteins occurs when an egg is cooked. Any source of energy can cause denaturation of proteins and is thus potentially dangerous to living organisms. For example, ultraviolet and X-ray radiation or nuclear radioactivity can disrupt protein structure, which may lead to cancer or genetic damage. Protein damage is also caused by chemicals like benzene, trichloroethane, and 1,2-dibromoethane. The metals lead and mercury, which have a very high affinity for sulfur, cause protein denaturation by disrupting disulfide bonds between protein chains.

The tremendous flexibility in the various levels of protein structure allows the tailoring of proteins for a wide range of specific functions. Proteins are the “work-horse” molecules of living organisms.

Carbohydrates

Carbohydrates form another class of biologically important molecules. They serve as a food source for most organisms and as a structural material for plants. Because many carbohydrates have the empirical formula CH_2O , it was originally believed that these substances were hydrates of carbon, thus accounting for the name.

Most important carbohydrates, such as starch and cellulose, are polymers composed of monomers called **monosaccharides**, or **simple sugars**. The monosaccharides are polyhydroxy ketones and aldehydes. The most important contain five carbon atoms (**pentoses**) or six carbon atoms (**hexoses**). One important hexose is *fructose*, a sugar found in honey and fruit. Its structure is

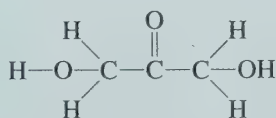
**FIGURE 22.25**

The permanent waving of hair.

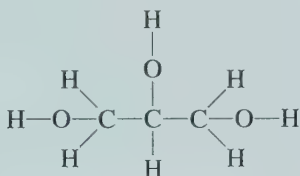
where the asterisks indicate chiral carbon atoms. In Section 21.4 we saw that molecules with nonsuperimposable mirror images exhibit optical isomerism. A carbon

Tanning in the Shade

Among today's best-selling cosmetics are self-tanning lotions. Many light-skinned people want to look like they have just spent a vacation in the Caribbean, but they recognize the dangers of too much sun—it causes premature aging and may lead to skin cancer. Chemistry has come to the rescue in the form of lotions that produce an authentic-looking tan. All of these lotions have the same active ingredient: dihydroxyacetone (DHA), DHA, which has the structure



is a nontoxic, simple sugar that occurs as an intermediate in carbohydrate metabolism in higher-order plants and animals. The DHA used in self-tanners is prepared by bacterial fermentation of glycerine,



The tanning effects of DHA were discovered by accident in the 1950s at Children's Hospital at the University of Cincinnati, where DHA was being used to treat children with glycogen storage disease. When the DHA was accidentally spilled on the skin, it produced brown spots.

The mechanism of the browning process involves the Maillard reaction, which was discovered by Louis-Camille Maillard in 1912. In this process amino acids react with sugars to create brown or golden brown products. The same reaction is responsible for much of the browning that occurs during the manufacture and storage of foods. It is also the reason that beer is golden brown.

The browning of skin occurs in the stratum corneum—the outermost, dead layer—where the DHA reacts with free amino ($-\text{NH}_2$) groups of the proteins found there.

DHA is present in most tanning lotions at concentrations between 2% and 5%, although some products designed to give a deeper tan are more concentrated. Because the lotions themselves turn brown above pH 7, the tanning lotions are buffered at pH 5.

Thanks to these new products, tanning is now both safe and easy.



Ingredients: Water, Aloe Vera Gel, Glycerin, Propylene Glycol, Polysorbate 20, Fragrance, Tocopheryl Acetate (Vitamin E Acetate), Imidazolidinyl Urea, Dihydroxyacetone.

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www.coppertone.com

21621-C



Self-tanning products and a close-up of a label showing the contents.

General Name of Sugar	Number of Carbon Atoms
Triose	3
Tetrose	4
Pentose	5
Hexose	6
Heptose	7
Octose	8
Nonose	9

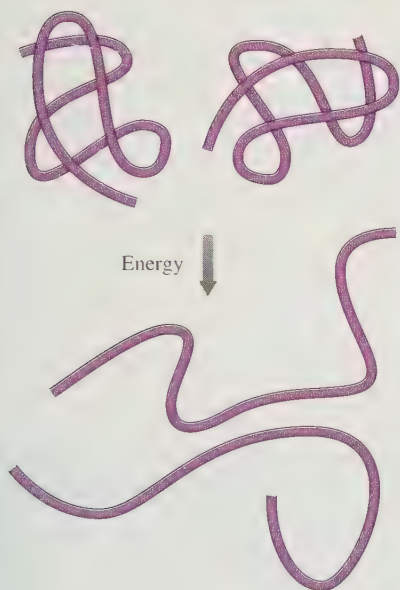
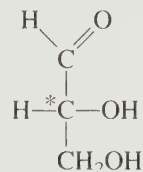


FIGURE 22.26
A schematic representation of the thermal denaturation of a protein.

TABLE 22.8 Some Important Monosaccharides

Pentoses			
D-Ribose	D-Arabinose	D-Ribulose	
$\begin{array}{c} \text{CHO} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$	$\begin{array}{c} \text{CHO} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$	$\begin{array}{c} \text{CH}_2\text{OH} \\ \\ \text{C}=\text{O} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$	
Hexoses			
D-Glucose	D-Mannose	D-Galactose	D-Fructose
$\begin{array}{c} \text{CHO} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$	$\begin{array}{c} \text{CHO} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$	$\begin{array}{c} \text{CH}_2\text{OH} \\ \\ \text{C}=\text{O} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$	$\begin{array}{c} \text{CH}_2\text{OH} \\ \\ \text{C}=\text{O} \\ \\ \text{HO}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$

atom with four *different* groups bonded to it in a tetrahedral arrangement *always* has a nonsuperimposable mirror image (see Fig. 22.27, which gives rise to a pair of optical isomers. For example, the simplest sugar, glyceraldehyde,

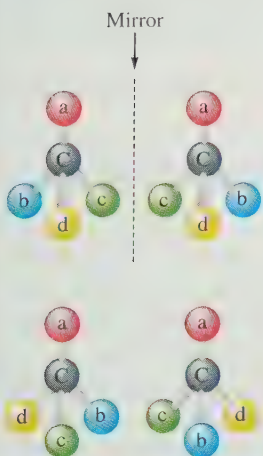


which has one chiral carbon, has two optical isomers, as shown in Fig. 22.28 on page 1082.

In fructose each of the three chiral carbon atoms satisfies the requirement of being surrounded by four different groups. This leads to a total of 2^3 , or 8, isomers that differ in their ability to rotate polarized light. The particular isomer whose structure is shown in Table 22.8 is called D-fructose. Generally, monosaccharides have one isomer that is more common in nature than the others. The most important pentoses and hexoses are shown in Table 22.8.

FIGURE 22.27

When a tetrahedral carbon atom has four different substituents, there is no way that its mirror image can be superimposed. The lower two forms show other possible orientations of the molecule. Compare these with the mirror image and note that they cannot be superimposed.



SAMPLE EXERCISE 22.9

Chiral Carbons in Carbohydrates

Determine the number of chiral carbon atoms in the following pentose:

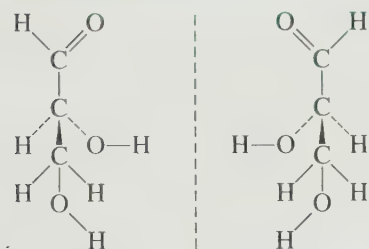
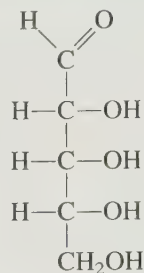


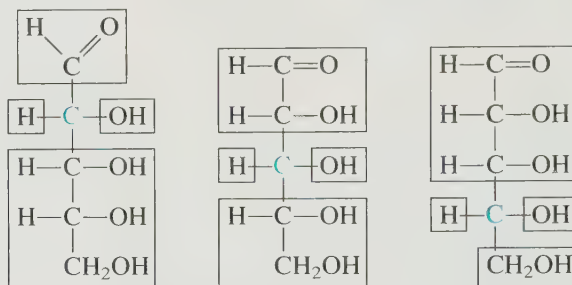
FIGURE 22.28

The mirror image optical isomers of glyceraldehyde. Note that these mirror images cannot be superimposed.



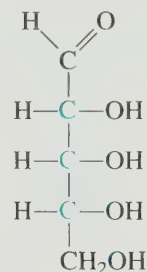
SOLUTION

We must look for carbon atoms that have four different substituents. The top carbon has only three substituents and thus cannot be chiral. The three carbon atoms shown in blue each have four different groups attached to them:



Since the fifth carbon atom has only three types of substituents (it has two hydrogen atoms), it is not chiral.

Thus the three chiral carbon atoms in this pentose are those shown in blue:



Note that D-ribose and D-arabinose, shown in Table 22.8, are two of the eight isomers of this pentose.

See Exercises 22.96 and 22.101 through 22.104.

Although we have so far represented the monosaccharides as straight-chain molecules, they usually cyclize, or form a ring structure, in aqueous solution. Figure 22.29 shows this reaction for fructose. Note that a new bond is formed between the oxygen of the terminal hydroxyl group and the carbon of the ketone group. In the cyclic form fructose is a five-membered ring containing a C—O—C bond. The same type of reaction can occur between a hydroxyl group and an aldehyde group, as shown for D-glucose in Fig. 22.30. In this case a six-membered ring is formed.

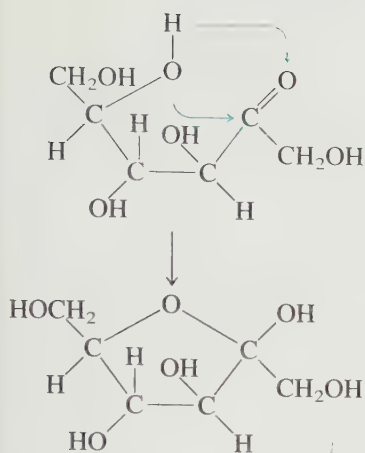


FIGURE 22.29
The cyclization of D-fructose.

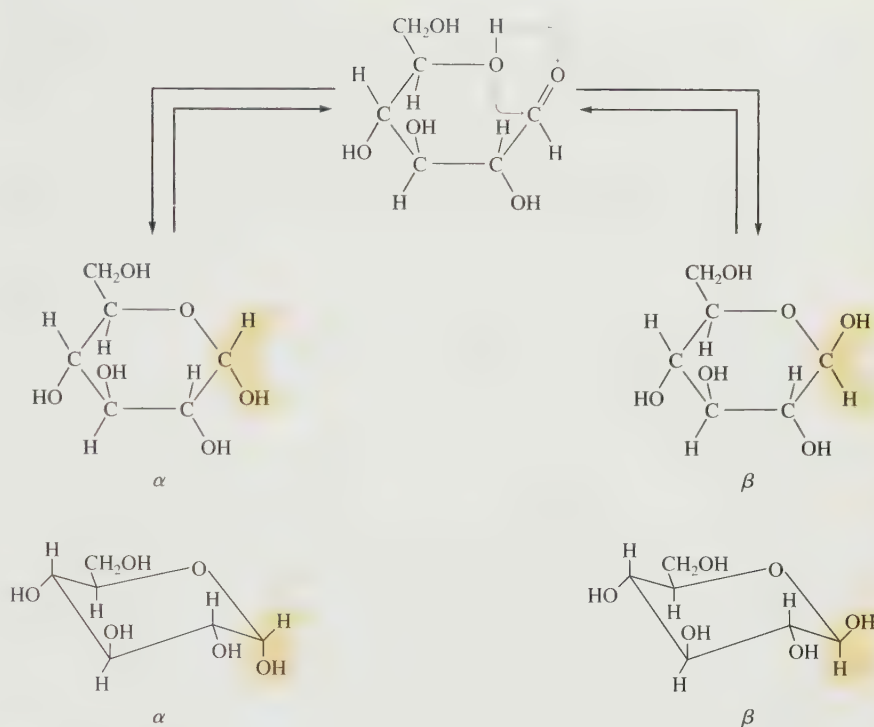


FIGURE 22.30

The cyclization of glucose. Two different rings are possible; they differ in the orientation of the hydroxy group and hydrogen on one carbon, as indicated. The two forms are designated α and β and are shown here in two representations.



Bowl of sugar cubes.

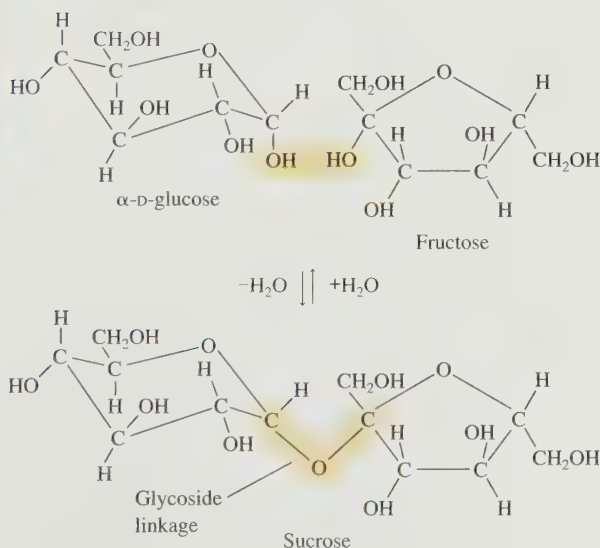
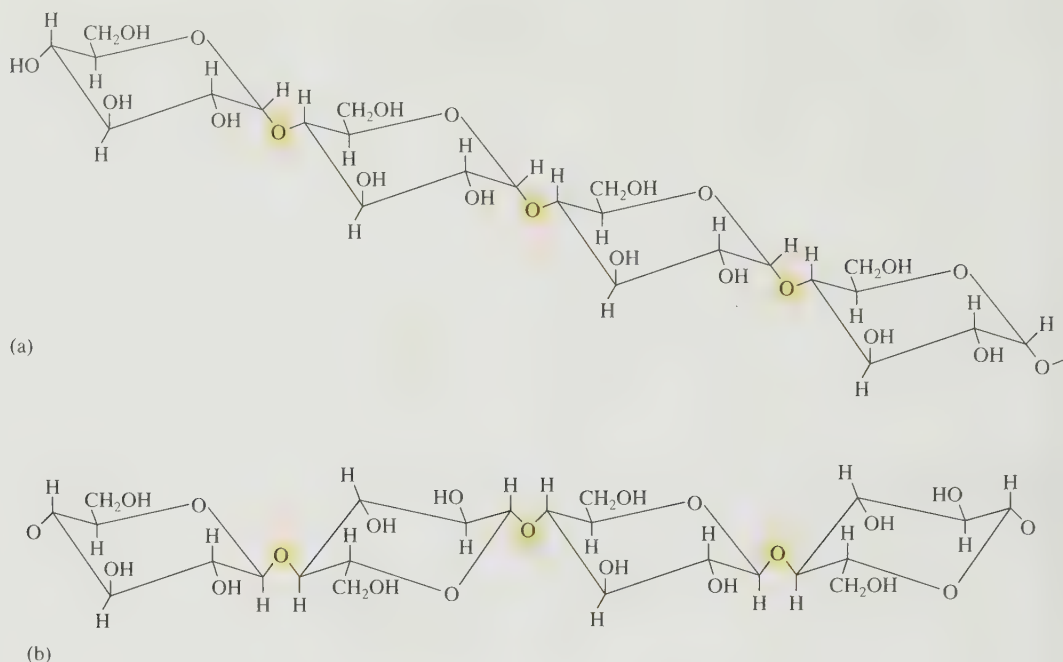


FIGURE 22.31
Sucrose is a disaccharide formed from α -D-glucose and fructose.

**FIGURE 22.32**

(a) The polymer amylose is a major component of starch and is made up of α -D-glucose monomers.

(b) The polymer cellulose, which consists of β -D-glucose monomers.

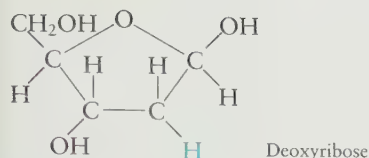
above reaction is reversed. An enzyme in saliva catalyzes the breakdown of this disaccharide.

Large polymers consisting of many monosaccharide units, called polysaccharides, can form when each ring forms two glycoside linkages, as shown in Fig. 22.32. Three of the most important of these polymers are starch, cellulose, and glycogen. All these substances are polymers of glucose, differing from each other in the nature of the glycoside linkage, the amount of branching, and molecular weight (molar mass).

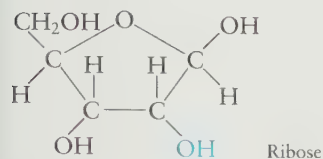
Starch, a polymer of α -D-glucose, consists of two parts: *amylose*, a straight-chain polymer of α -glucose [see Fig. 22.32(a)], and *amylopectin*, a highly branched polymer of α -glucose with a molecular weight that is 10 to 20 times that of amylose. Branching occurs when a third glycoside linkage attaches a branch to the main polymer chain.

Starch, the carbohydrate reservoir in plants, is the form in which glucose is stored by the plant for later use as cellular fuel. Glucose is stored in this high-molecular-weight form because it results in less stress on the plant's internal structure by osmotic pressure. Recall from Section 11.6 that it is the concentration of solute molecules (or ions) that determines the osmotic pressure. Combining the individual glucose molecules into one large chain keeps the concentration of solute molecules relatively low, minimizing the osmotic pressure.

Cellulose, the major structural component of woody plants and natural fibers (such as cotton), is a polymer of β -D-glucose and has the structure shown in Fig. 22.32(b). Note that the β -glycoside linkages in cellulose give the glucose rings a different relative orientation than is found in starch. Although this difference may seem minor, it has very important consequences. The human digestive system contains α -glycosidases, enzymes that can catalyze breakage of the α -glycoside bonds in starch. These enzymes are not effective on the β -glycoside bonds of cellulose, presumably because the different structure results in a poor fit between the enzyme's



(a)



(b)

FIGURE 22.33

The structure of the pentoses (a) deoxyribose and (b) ribose. Deoxyribose is the sugar molecule present in DNA; ribose is found in RNA.

active site and the carbohydrate. The enzymes necessary to cleave β -glycoside linkages, the β -glycosidases, are found in bacteria that exist in the digestive tracts of termites, cows, deer, and many other animals. Thus, unlike humans, these animals can derive nutrition from cellulose.

Glycogen, the main carbohydrate reservoir in animals, has a structure similar to that of amylopectin but with more branching. It is this branching that is thought to facilitate the rapid breakdown of glycogen into glucose when energy is required.

Nucleic Acids

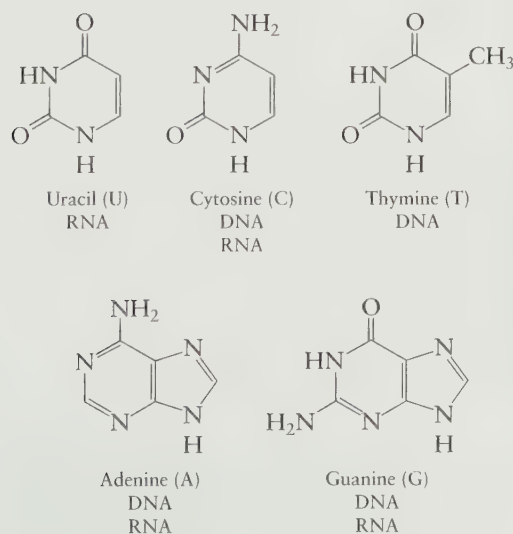
Life is possible only because each cell, when it divides, can transmit the vital information about how it works to the next generation. It has been known for a long time that this process involves the chromosomes in the nucleus of the cell. Only since 1953, however, have scientists understood the molecular basis of this intriguing cellular “talent.”

The substance that stores and transmits the genetic information is a polymer called **deoxyribonucleic acid (DNA)**, a huge molecule with a molecular weight as high as several billion grams per mole. Together with other similar nucleic acids called the **ribonucleic acids (RNA)**, DNA is also responsible for the synthesis of the various proteins needed by the cell to carry out its life functions. The RNA molecules, which are found in the cytoplasm outside the nucleus, are much smaller than DNA polymers, with molecular weights of only 20,000 to 40,000 grams per mole.

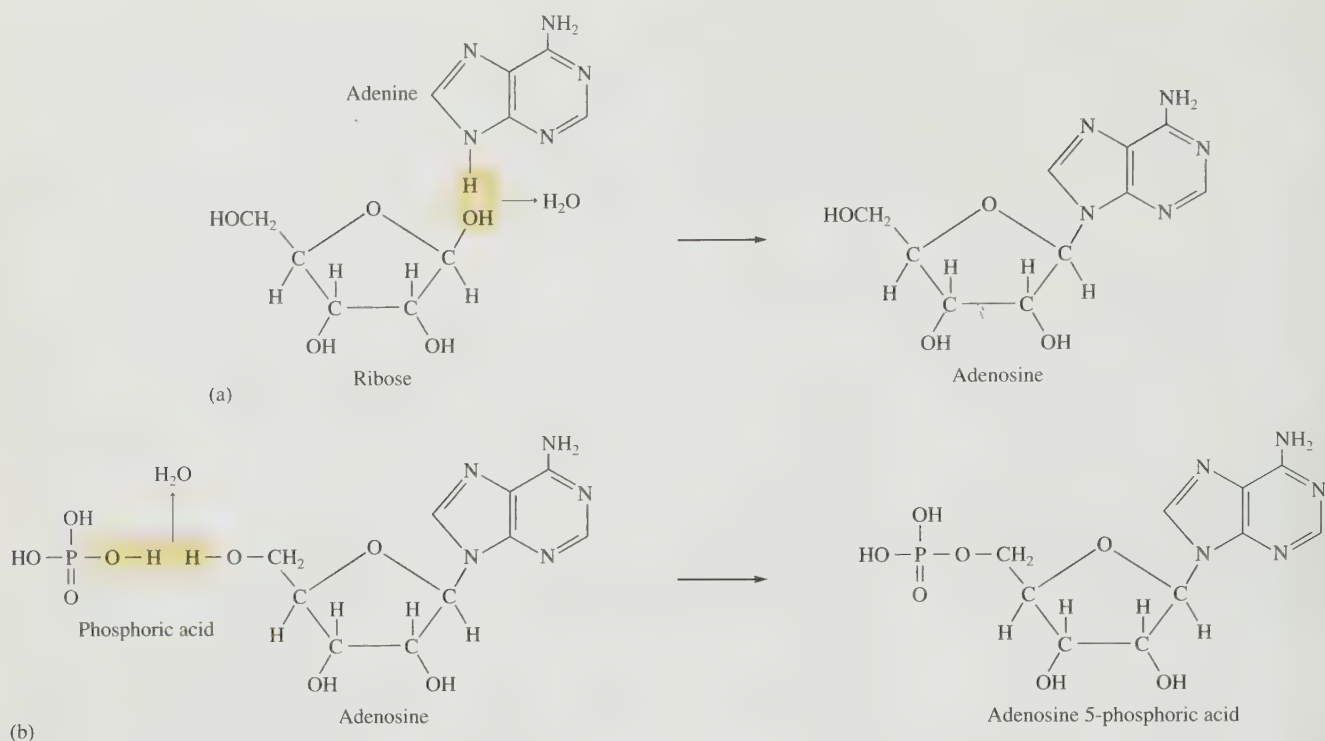
The monomers of the nucleic acids, called **nucleotides**, are composed of three distinct parts:

1. A *five-carbon sugar*, deoxyribose in DNA and ribose in RNA (Fig. 22.33)
2. A *nitrogen-containing organic base* of the type shown in Fig. 22.34
3. A *phosphoric acid molecule* (H_3PO_4)

The base and the sugar combine as shown in Fig. 22.35(a) to form a unit that in turn reacts with phosphoric acid to create the nucleotide, which is an ester [see Fig. 22.35(b)]. The nucleotides become connected through condensation reactions that

**FIGURE 22.34**

The organic bases found in DNA and RNA.

**FIGURE 22.35**

(a) Adenosine is formed by the reaction of adenine with ribose. (b) The reaction of phosphoric acid with adenosine to form the ester adenosine 5-phosphoric acid, a nucleotide. (At biological pH, the phosphoric acid would not be fully protonated as is shown here.)



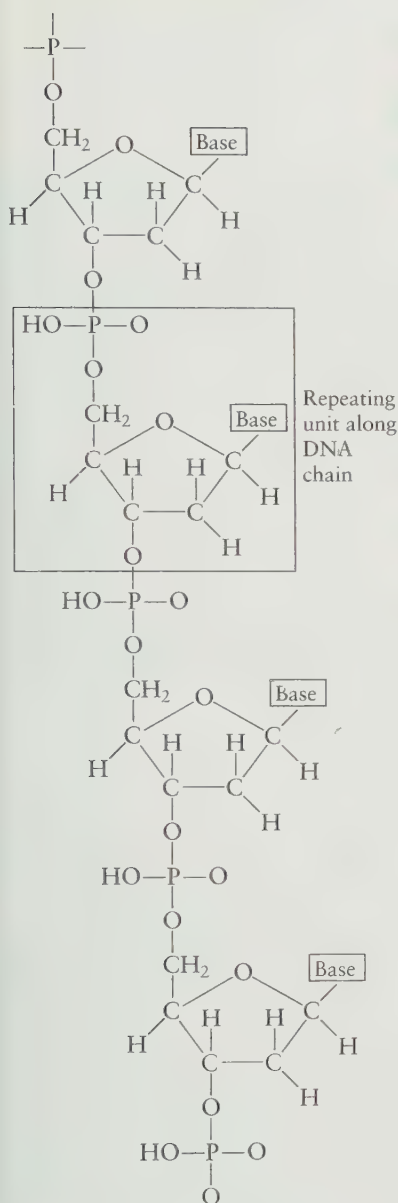
A computer image of the base pairs of DNA. The blue lines represent the sugar-phosphate backbone and the colored bars represent the hydrogen bonding between the base pairs.

eliminate water to give a polymer of the type represented in Fig. 22.36; such a polymer can contain a *billion* units.

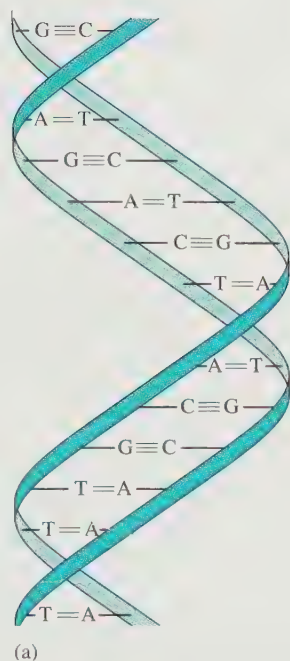
The key to DNA's functioning is its *double-helical structure with complementary bases on the two strands*. The bases form hydrogen bonds to each other, as shown in Fig. 22.37. Note that the structures of cytosine and guanine make them perfect partners for hydrogen bonding, and they are *always* found as pairs on the two strands of DNA. Thymine and adenine form similar hydrogen-bonding pairs.

There is much evidence to suggest that the two strands of DNA unwind during cell division and that new complementary strands are constructed on the unraveled strands (Fig. 22.38). Because the bases on the strands always pair in the same way—cytosine with guanine and thymine with adenine—each unraveled strand serves as a template for attaching the complementary bases (along with the rest of the nucleotide). This process results in two double-helix DNA structures that are identical to the original one. Each new double strand contains one strand from the original DNA double helix and one newly synthesized strand. This replication of DNA allows for the transmission of genetic information as the cells divide.

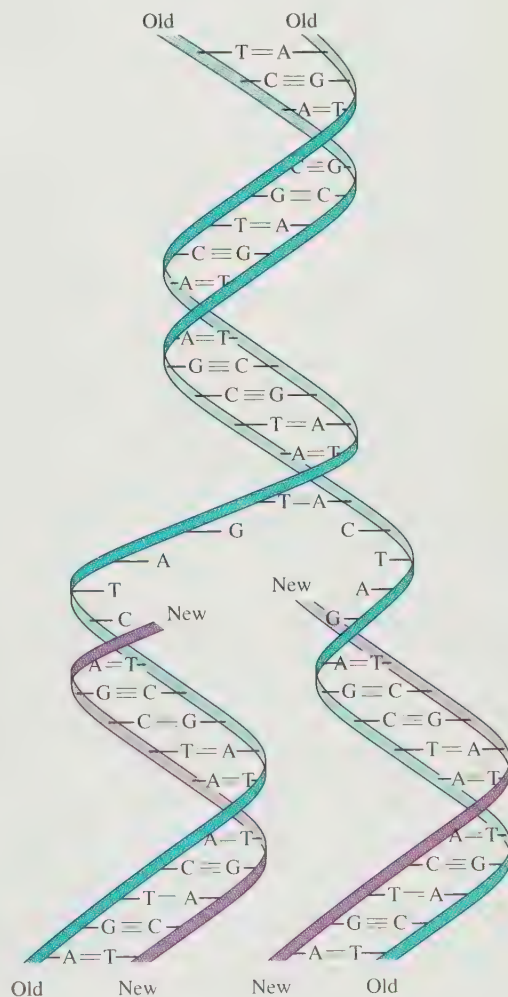
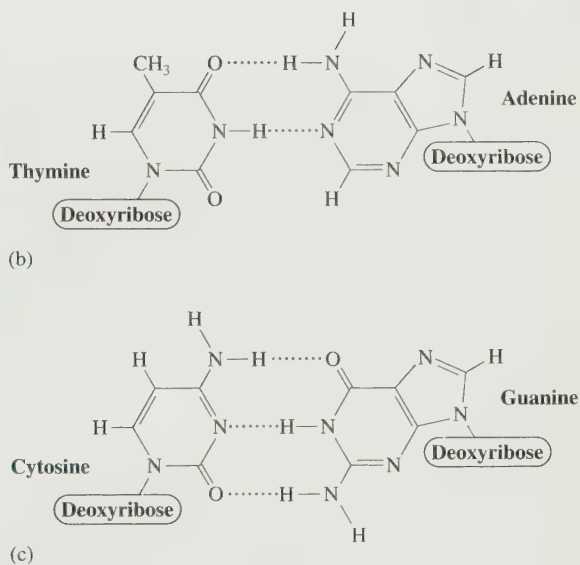
The other major function of DNA is **protein synthesis**. A given segment of the DNA, called a **gene**, contains the code for a specific protein. These codes transmit the primary structure of the protein (the sequence of amino acids) to the construction “machinery” of the cell. There is a specific code for each amino acid in the protein, which ensures that the correct amino acid will be inserted as the protein chain grows. A code consists of a set of three bases called a **codon**.

**FIGURE 22.36**

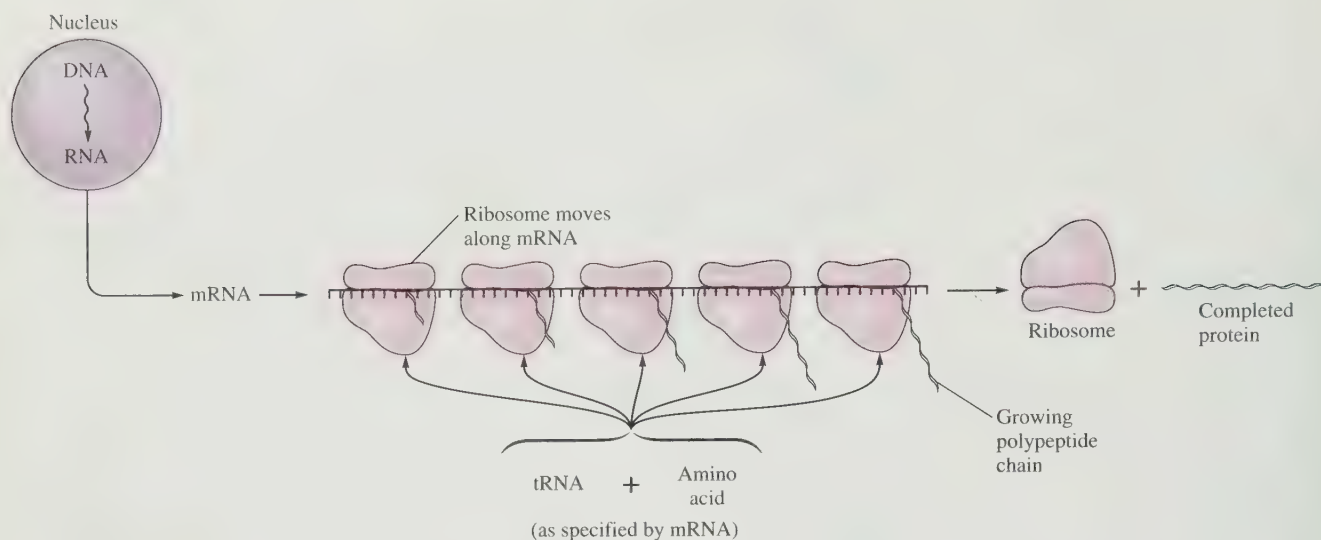
A portion of a typical nucleic acid chain. Note that the backbone consists of sugar-phosphate esters.

**FIGURE 22.37**

(a) The DNA double helix contains two sugar-phosphate backbones, with the bases from the two strands hydrogen-bonded to each other. The complementarity of the (b) thymine-adenine and (c) cytosine-guanine pairs.

**FIGURE 22.38**

During cell division the original DNA double helix unwinds and new complementary strands are constructed on each original strand.

**FIGURE 22.39**

The mRNA molecule, constructed from a specific gene on the DNA, is used as the pattern to construct a given protein with the assistance of ribosomes. The tRNA molecules attach to specific amino acids and put them in place as called for by the codons on the mRNA.

DNA stores the genetic information, while RNA molecules are responsible for transmitting this information to the ribosomes, where protein synthesis actually occurs. This complex process involves, first, the construction of a special RNA molecule called **messenger RNA (mRNA)**. The mRNA is built in the cell nucleus on the appropriate section of DNA (the gene); the double helix is “unzipped,” and the complementarity of the bases is used in a process similar to that used in DNA replication. The mRNA then migrates into the cytoplasm of the cell where, with the assistance of the ribosomes, the protein is synthesized.

Small RNA fragments, called **transfer RNA (tRNA)**, are tailored to find specific amino acids and then to attach them to the growing protein chain as dictated by the codons in the mRNA. Transfer RNA has a lower molecular weight than messenger RNA. It consists of a chain of 75 to 80 nucleotides, including the bases adenine, cytosine, guanine, and uracil, among others. The chain folds back onto itself in various places as the complementary bases along the chain form hydrogen bonds. The tRNA decodes the genetic message from the mRNA, using a complementary triplet of bases called an **anticodon**. The nature of the anticodon governs which amino acid will be brought to the protein under construction.

The protein is built in several steps. First, a tRNA molecule brings an amino acid to the mRNA [the anticodon of the tRNA must complement the codon of the mRNA (see Fig. 22.39)]. Once this amino acid is in place, another tRNA moves to the second codon site of the mRNA with its specific amino acid. The two amino acids link via a peptide bond, and the tRNA on the first codon breaks away. The process is repeated down the chain, always matching the tRNA anticodon with the mRNA codon.

For Review

Summary

The study of carbon-containing compounds and their properties is called organic chemistry. Most organic compounds contain chains or rings of carbon atoms. The organic molecules responsible for maintaining and reproducing life are called biomolecules.

Hydrocarbons are organic compounds composed of carbon and hydrogen. Those that contain only C—C single bonds are saturated and are called alkanes. All alkanes can be represented by the general formula C_nH_{2n+2} .

Methane (CH_4) is the simplest alkane, and the next three in the series are ethane (C_2H_6), propane (C_3H_8), and butane (C_4H_{10}). In a saturated hydrocarbon, each carbon atom is bonded to four other atoms and is described as being sp^3 hybridized. Alkanes containing long chains of carbon atoms are called normal, or straight-chain, hydrocarbons.

Structural isomerism in alkanes involves formation of branched structures. Specific rules for systematically naming alkanes indicate the point of attachment of any substituent group, the length of the root chain, and so on.

Alkanes can undergo combustion reactions to form carbon dioxide and water or substitution reactions in which hydrogen atoms are replaced by other atoms. Alkanes also can undergo dehydrogenation to form unsaturated hydrocarbons. Cyclic alkanes are saturated hydrocarbons with ring structures.

Hydrocarbons with carbon–carbon double bonds are called alkenes and are said to be unsaturated. The simplest alkene is ethylene (C_2H_4), which is described in terms of sp^2 hybridized carbon atoms. Because the p orbitals on the carbon atoms in ethylene form a π bond, free rotation of the two CH_2 groups relative to each other does not occur (as it does in alkanes). This restriction means that alkenes exhibit *cis–trans* isomerism.

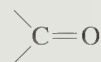
Alkynes are unsaturated hydrocarbons with a triple carbon–carbon bond. The simplest in the series is acetylene (C_2H_2), which is described as containing sp hybridized carbon atoms.

Unsaturated hydrocarbons undergo addition reactions such as hydrogenation (addition of hydrogen) and halogenation (addition of halogen atoms). Ethylene and substituted ethylene molecules can undergo polymerization, a process by which many molecules (monomers) are joined together to form a large chainlike molecule.

Aromatic hydrocarbons, such as benzene, are stable ring compounds with delocalized π electron systems. They undergo substitution reactions rather than the addition reactions characteristic of typical alkenes.

Organic molecules that contain elements in addition to carbon and hydrogen can be viewed as hydrocarbon derivatives: hydrocarbons with functional groups. Each functional group exhibits characteristic chemical properties.

Alcohols contain the —OH group and tend to have strong hydrogen bonding in the liquid state. Aldehydes and ketones contain the carbonyl group:



In aldehydes this group is bonded to at least one hydrogen atom. Carboxylic acids are characterized by the carboxyl group:

Key Terms

biomolecule
organic chemistry

Section 22.1

hydrocarbons
saturated
unsaturated
alkanes
normal (straight-chain or un-
branched) hydrocarbons
structural isomerism
combustion reaction
substitution reaction
dehydrogenation reaction
cyclic alkanes

Section 22.2

alkenes
cis–trans isomerism
alkynes
addition reaction
hydrogenation reaction
halogenation
polymerization

Section 22.3

aromatic hydrocarbons
phenyl group

Section 22.4

hydrocarbon derivatives
functional group
alcohols
phenol
carbonyl group
ketones
aldehydes
carboxylic acids
carboxyl group
ester
amines

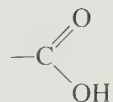
Section 22.5

polymers
thermoset polymer
thermoplastic polymer
crosslinking
vulcanization
addition polymerization
free radical

condensation polymerization
 copolymer
 homopolymer
 dimer
 polyester
 isotactic chain
 syndiotactic chain
 atactic chain
 polystyrene
 polyvinyl chloride (PVC)

Section 22.6

proteins
 fibrous proteins
 globular proteins
 α -amino acids
 side chains
 dipeptide
 peptide linkage
 polypeptide
 primary structure
 secondary structure
 α -helix
 pleated sheet
 random-coil arrangement
 tertiary structure
 disulfide linkage
 denaturation
 carbohydrates
 monosaccharides (simple sugars)
 pentoses
 hexoses
 sucrose
 disaccharide
 glycoside linkage
 starch
 cellulose
 glycogen
 deoxyribonucleic acid (DNA)
 ribonucleic acid (RNA)
 nucleotides
 protein synthesis
 gene
 codon
 messenger RNA (mRNA)
 transfer RNA (tRNA)
 anticodon



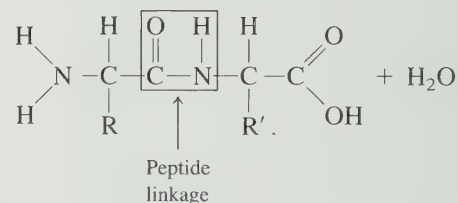
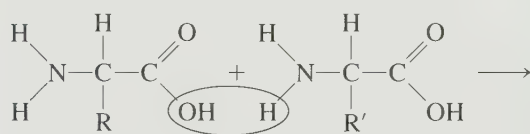
They can react with alcohols to form esters. Amines can be thought of as derivatives of ammonia in which one or more N—H bonds have been replaced by an N—C bond.

Polymers can be formed by addition polymerization in which monomers add together via a free radical mechanism. Polymers also can be formed by condensation polymerization, which involves the splitting out of a small molecule (often water) between two monomers to form a dimer, which then undergoes further condensation.

Proteins are a class of natural polymers with molecular weights ranging from 6000 to 1,000,000. Fibrous proteins are employed in the human body for structural purposes in muscle, hair, and cartilage. Globular proteins are molecules that transport and store oxygen and nutrients, act as catalysts, help regulate the body's systems, fight foreign objects, and so on.

The building blocks of proteins are the α -amino acids, which can be divided into polar and nonpolar classes, depending on whether the side chain (the R group) attached to the α -carbon is hydrophilic or hydrophobic.

A protein polymer is built by successive condensation reactions that produce peptide linkages:



The order or sequence of amino acids in the protein chain is called the primary structure. Differences in primary structure are what tailor proteins for specific functions.

The secondary structure refers to the arrangement of the protein chain, which is determined to a large extent by hydrogen bonding between atoms on different amino acids. When such interactions occur within the chain, a spiral structure called an α -helix results. When the hydrogen bonds are between different chains, a pleated sheet results. The overall shape of the protein is called its tertiary structure. The breakdown of tertiary protein structure, called denaturation, can be caused by energy sources or a variety of chemicals.

Carbohydrates serve as food sources for most organisms and as structural materials for plants. Simple carbohydrates, called monosaccharides, are most commonly five-carbon and six-carbon polyhydroxy ketones and aldehydes that contain chiral carbon atoms. Monosaccharides combine to form more complex carbohydrates. For example, sucrose is a disaccharide, and starch and cellulose are polymers of D-glucose.

When a cell divides, the genetic information is transmitted via deoxyribonucleic acid (DNA), which has a double helical structure whose two strands are held together by hydrogen bonding between pairs of organic bases—one from each strand. The bases occur only in specific pairs. During cell division, the double helix unravels, and a new polymer forms along each strand of the original DNA to form two double helical DNA molecules. The DNA contains segments called genes, which store the structural information for specific proteins. Various types of ribonucleic acid (RNA) molecules assist in protein synthesis.

A blue question or exercise number indicates that the answer to that question or exercise appears at the back of this book and a solution appears in the *Solutions Guide*.

Questions

- The normal (unbranched) hydrocarbons are often referred to as the *straight-chain hydrocarbons*. What does this name refer to? Does this mean that the carbon atoms in a straight-chain hydrocarbon really have a linear arrangement? Explain.
- A general rule for a group of hydrocarbon isomers is that as the amount of branching increases, the boiling point decreases. Explain why this would be true.
- Distinguish between *isomerism* and *resonance*.
- Distinguish between structural and geometrical isomerism.
- Distinguish between substitution and addition reactions. Give an example of each type.
- Define and give an example of each of the following.
 - addition polymer
 - condensation polymer
 - copolymer
- Distinguish between a thermoset polymer and a thermoplastic polymer.
- How do the physical properties of polymers depend on chain length and extent of chain branching?
- Explain how crosslinking agents are used to change the physical properties of polymers.
- Isotactic polypropylene makes stronger fibers than atactic polypropylene. Explain.
- Nylon is named according to the number of C atoms between the N atoms in the chain. Nylon-46 has 4 C atoms then 6 C atoms, and this pattern repeats. Nylon-6 always has 6 atoms in a row. Speculate as to why nylon-46 is stronger than nylon-6. (*Hint*: Consider the strengths of interchain forces.)
- In which polymer, polyethylene or polyvinyl chloride, would you expect to find the stronger intermolecular forces (assuming the average chain lengths are equal)?
- Distinguish between the primary, secondary, and tertiary structures of a protein. Give examples of the types of forces that maintain each type of structure.
- Describe how denaturation affects the function of a protein.
- Aqueous solutions of amino acids are buffered solutions. Explain.

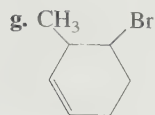
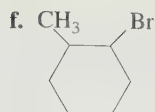
- What is a *disaccharide*? What monosaccharide units make up the disaccharide sucrose? What is the bond called that forms between the monosaccharide units?
- What forces are responsible for the solubility of starch in water?
- What is optical isomerism? What do you look for to determine whether an organic compound exhibits optical isomerism?
- The compounds adenine, guanine, cytosine, and thymine are called the nucleic acid bases. What structural features in these compounds make them bases?
- Describe the structural differences between DNA and RNA.
- The deletion of a single base from a DNA molecule can constitute a fatal mutation. Substitution of one base for another is often not as serious a mutation. Explain.
- Describe the complementary base pairing between the two individual strands of DNA that forms the overall double-helical structure. How is complementary base pairing involved in the replication of the DNA molecule during cell division?

Exercises

In this section similar exercises are paired.

Hydrocarbons

- Draw the five structural isomers of hexane (C_6H_{14}).
- Name the structural isomers in Exercise 23.
- Draw all the structural isomers for C_8H_{18} that have the following root name (longest carbon chain). Name the structural isomers.
 - heptane
 - butane
- Draw all the structural isomers for C_8H_{18} that have the following root name (longest carbon chain). Name the structural isomers.
 - hexane
 - pentane
- Draw the structural formula for each of the following.
 - 2-methylpentane
 - 2,2,4-trimethylpentane, also called *isooctane*. This substance is the reference (100 level) for octane ratings.
 - 2-*tert*-butylpentane
 - The name given in part c is incorrect. Give the correct name for this hydrocarbon.



Isomerism

39. Which of the compounds in Exercises 31 and 33 exhibit *cis-trans* isomerism?
40. Which of the compounds in Exercises 32 and 34 exhibit *cis-trans* isomerism?
41. Draw all the structural isomers of C_5H_{10} . Ignore any cyclic isomers.
42. Which of the structural isomers in Exercise 41 exhibit *cis-trans* isomerism?
43. Draw all the structural and geometrical (*cis-trans*) isomers of C_3H_5Cl .
44. Draw all the structural and geometrical (*cis-trans*) isomers of bromochloropropene.
45. Draw all structural and geometrical (*cis-trans*) isomers of C_4H_7F . Ignore any cyclic isomers.
46. *Cis-trans* isomerism is also possible in molecules with rings. Draw the *cis* and *trans* isomers of 1,2-dimethylcyclohexane. In Exercise 45, you drew all of the noncyclic structural and geometric isomers of C_4H_7F . Now draw the cyclic structural and geometric isomers of C_4H_7F .

47. Draw the following.

- a. *cis*-2-hexene
- b. *trans*-2-butene
- c. *cis*-2,3-dichloro-2-pentene

48. Name the following compounds.

- a.
- b.
- c.

49. If one hydrogen in a hydrocarbon is replaced by a halogen atom, the number of isomers that exist for the substituted compound depends on the number of types of hydrogen in the original hydrocarbon. Thus there is only one form of chloroethane (all hydrogens in ethane are equivalent), but

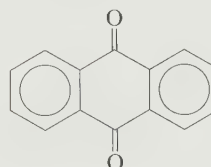
there are two isomers of propane that arise from the substitution of a methyl hydrogen or a methylene hydrogen. How many isomers can be obtained when one hydrogen in each of the compounds named below is replaced by a chlorine atom?

- a. *n*-pentane
 - b. 2-methylbutane
 - c. 2,4-dimethylpentane
 - d. methylcyclobutane
50. There are three isomers of dichlorobenzene, one of which has now replaced naphthalene as the main constituent of mothballs.
- a. Identify the *ortho*, the *meta*, and the *para* isomers of dichlorobenzene.
 - b. Predict the number of isomers for trichlorobenzene.
 - c. It turns out that the presence of one chlorine atom on a benzene ring will cause the next substituent to add *ortho* or *para* to the first chlorine atom on the benzene ring. What does this tell you about the synthesis of *m*-dichlorobenzene?
 - d. Which of the isomers of trichlorobenzene will be the hardest to prepare?

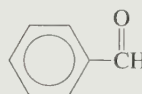
Functional Groups

51. Identify each of the following compounds as a carboxylic acid, ester, ketone, aldehyde, or amine.

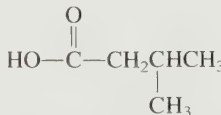
- a. Anthraquinone, an important starting material in the manufacture of dyes:



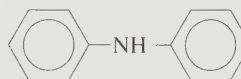
b.



c.

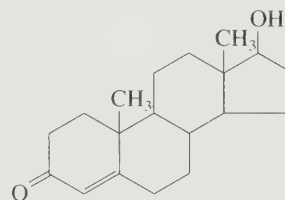


d.

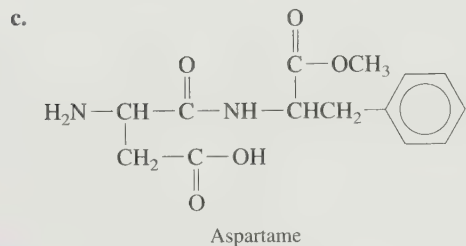
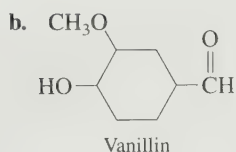


52. Identify the functional groups present in the following compounds.

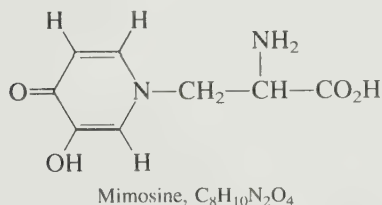
a.



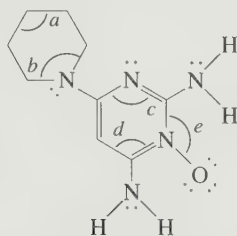
Testosterone



53. Mimosine is a natural product found in large quantities in the seeds and foliage of some legume plants and has been shown to cause inhibition of hair growth and hair loss in mice.

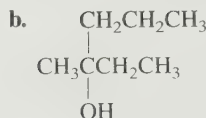
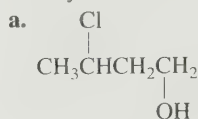


- What functional groups are present in mimosine?
 - Give the hybridization of the eight carbon atoms in mimosine.
 - How many σ and π bonds are found in mimosine?
54. Minoxidil ($C_9H_{15}N_5O$) is a compound produced by Pharmacia Company that has been approved as a treatment of some types of male pattern baldness.



- Would minoxidil be more soluble in acidic or basic aqueous solution? Explain.
- Give the hybridization of the five nitrogen atoms in minoxidil.
- Give the hybridization of each of the nine carbon atoms in minoxidil.
- Give approximate values of the bond angles marked *a*, *b*, *c*, *d*, and *e*.
- Including all the hydrogen atoms, how many σ bonds exist in minoxidil?
- How many π bonds exist in minoxidil?

55. For each of the following alcohols, give the systematic name and specify whether the alcohol is primary, secondary, or tertiary.



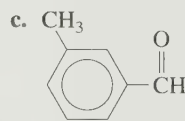
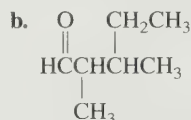
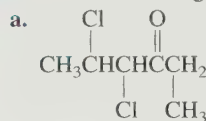
56. Draw structural formulas for each of the following alcohols. Indicate whether the alcohol is primary, secondary, or tertiary.

- 1-butanol
- 2-butanol
- 2-methyl-1-butanol
- 2-methyl-2-butanol

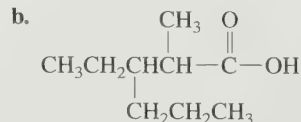
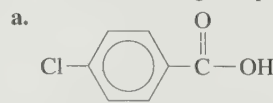
57. Name all the alcohols that have the formula $C_5H_{12}O$. How many ethers have the formula $C_5H_{12}O$?

58. Name all the aldehydes and ketones that have the formula $C_5H_{10}O$.

59. Name the following compounds.



60. Name the following compounds.

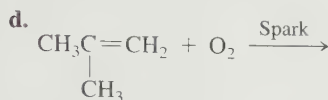
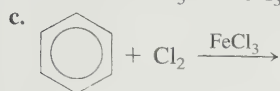
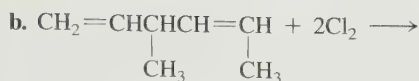


- c. $HCOOH$

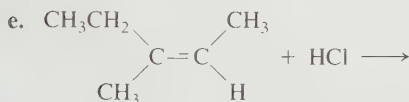
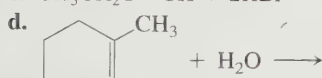
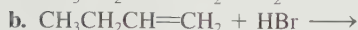
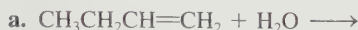
Reactions of Organic Compounds

61. Complete the following reactions.





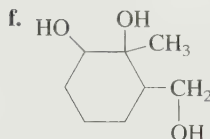
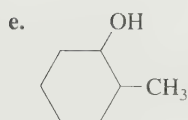
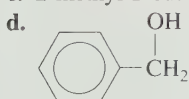
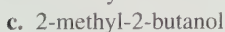
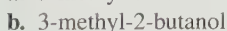
62. Reagents such as HCl, HBr, and HOH (H_2O) can add across carbon-carbon double and triple bonds, with H forming a bond to one of the carbon atoms in the multiple bond and Cl, Br, or OH forming a bond to the other carbon atom in the multiple bond. In some cases, two products are possible. For the major organic product, the addition occurs so that the hydrogen atom in the reagent attaches to the carbon atom in the multiple bond that already has the greater number of hydrogen atoms bonded to it. With this rule in mind, draw the structure of the major product in each of the following reactions.



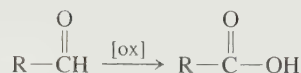
63. When toluene ($\text{C}_6\text{H}_5\text{CH}_3$) reacts with chlorine gas in the presence of iron(III) catalyst, the product is a mixture of the *ortho* and *para* isomers of $\text{C}_6\text{H}_4\text{ClCH}_3$. However, when the reaction is light-catalyzed with no Fe^{3+} catalyst present, the product is $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$. Explain.

64. Why is it preferable to produce chloroethane by the reaction of $\text{HCl}(\text{g})$ with ethene than by the reaction of $\text{Cl}_2(\text{g})$ with ethane? (See Exercise 62.)

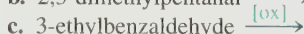
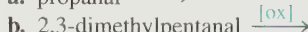
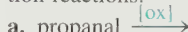
65. Using appropriate reactants, alcohols can be oxidized into aldehydes, ketones, and/or carboxylic acids. Primary alcohols can be oxidized into aldehydes, which can then be oxidized into carboxylic acids. Secondary alcohols can be oxidized into ketones, while tertiary alcohols do not undergo this type of oxidation. Give the structure of the product(s) resulting from the oxidation of each of the following alcohols.



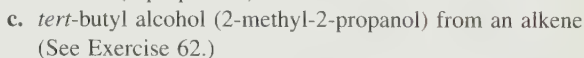
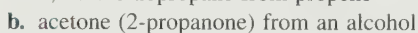
66. Oxidation of an aldehyde yields a carboxylic acid:



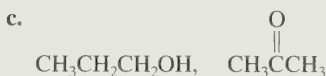
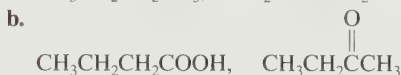
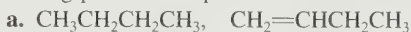
Draw the structures for the products of the following oxidation reactions.



67. How would you synthesize each of the following?



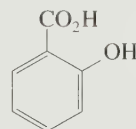
68. What tests could you perform to distinguish between the following pairs of compounds?



69. How would you synthesize the following esters?



70. Salicylic acid has the following structure:

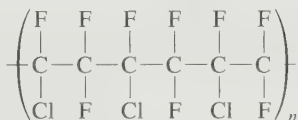


Since salicylic acid has both an alcohol functional group and a carboxylic acid functional group, it can undergo two different esterification reactions depending on which functional group reacts. For example, when treated with ethanoic acid (acetic acid), salicylic acid behaves as an alcohol and the ester produced is acetylsalicylic acid (aspirin). On the other hand, when reacted with methanol, salicylic acid behaves as

an acid and the ester methyl salicylate (oil of wintergreen) is produced. Methyl salicylate is also an analgesic and part of the formulation of many liniments for sore muscles. What are the structures of acetylsalicylic acid and methyl salicylate?

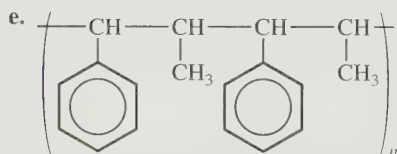
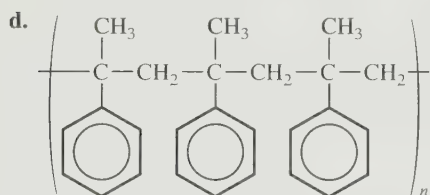
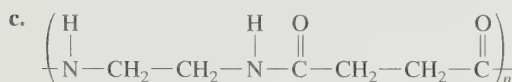
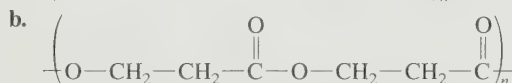
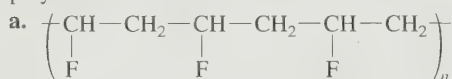
Polymers

71. Kel-F is a polymer with the structure

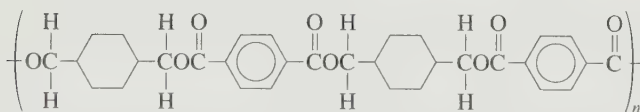


What is the monomer for Kel-F?

72. What monomer(s) must be used to produce the following polymers?



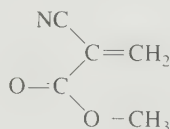
g.



(This polymer is Kodel, used to make fibers of stain-resistant carpeting.)

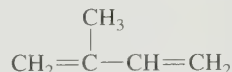
Classify these polymers as condensation or addition polymers. Which are copolymers?

73. "Super glue" contains methyl cyanoacrylate,

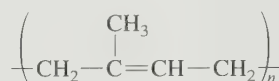


which readily polymerizes upon exposure to traces of water or alcohols on the surfaces to be bonded together. The polymer provides a strong bond between the two surfaces. Draw the structure of the polymer formed by methyl cyanoacrylate.

74. Isoprene is the repeating unit in natural rubber. The structure of isoprene is

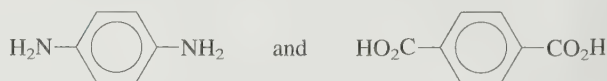


- a. Give a systematic name for isoprene.
b. When isoprene is polymerized, two polymers of the form



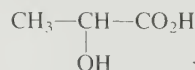
are possible. In natural rubber, the *cis* configuration is found. The polymer with the *trans* configuration about the double bond is called gutta percha and was once used in the manufacture of golf balls. Draw the structure of natural rubber and gutta percha showing three repeating units and the configuration about the carbon-carbon double bonds.

75. Kevlar, used in bulletproof vests, is made by the condensation copolymerization of the monomers



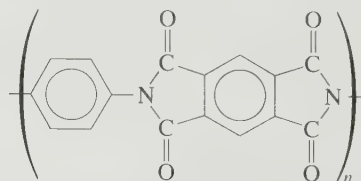
Draw the structure of a portion of the Kevlar chain.

76. The polyester formed from lactic acid,

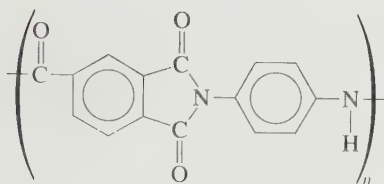


is used for tissue implants and surgical sutures that will dissolve in the body. Draw the structure of a portion of this polymer.

77. Polyimides are polymers that are tough and stable at temperatures of up to 400°C. They are used as a protective coating on the quartz fibers used in fiber optics. What monomers were used to make the following polyimide?

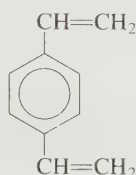


78. The Amoco Chemical Company has successfully raced a car with a plastic engine. Many of the engine parts, including piston skirts, connecting rods, and valve-train components, were made of a polymer called *Torlon*:



What monomers are used to make this polymer?

79. Polystyrene can be made more rigid by copolymerizing styrene with divinylbenzene:



How does the divinylbenzene make the copolymer more rigid?

80. Polyesters containing double bonds are often crosslinked by reacting the polymer with styrene.

a. Draw the structure of the copolymer of



b. Draw the structure of the crosslinked polymer (after the polyester has been reacted with styrene).

81. Which of the following polymers would be stronger or more rigid? Explain your choices.

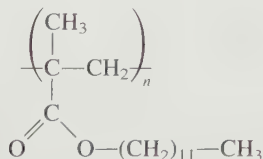
a. The copolymer of ethylene glycol and terephthalic acid or the copolymer of 1,2-diaminoethane and terephthalic acid (1,2-diaminoethane = $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$)

b. The polymer of $\text{HO}-(\text{CH}_2)_6-\text{CO}_2\text{H}$ or that of



c. Polyacetylene or polyethylene (The monomer in polyacetylene is ethyne.)

82. Poly(lauryl methacrylate) is used as an additive in motor oils to counter the loss of viscosity at high temperature. The structure is



The long hydrocarbon chain of poly(lauryl methacrylate) makes the polymer soluble in oil (a mixture of hydrocarbons with mostly 12 or more carbon atoms). At low temperatures the polymer is coiled into balls. At higher temperatures the balls uncoil and the polymer exists as long chains. Explain how this helps control the viscosity of oil.

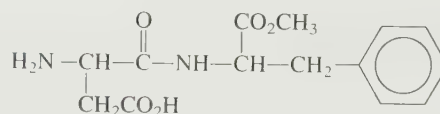
Natural Polymers

83. Which of the amino acids in Fig. 22.18 contain the following functional groups in their R group?

a. alcohol c. amine
b. carboxylic acid d. amide

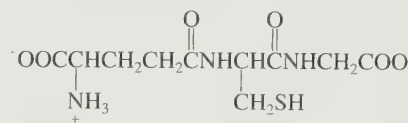
84. When pure crystalline amino acids are heated, decomposition generally occurs before the solid melts. Account for this observation. (Hint: Crystalline amino acids exist as $\text{H}_3\text{N}^+\text{NCRHCOO}^-$, called *zwitterions*.)

85. Aspartame, the artificial sweetener marketed under the name Nutra-Sweet, is a methyl ester of a dipeptide:



- a. What two amino acids are used to prepare aspartame?
b. There is concern that methanol may be produced by the decomposition of aspartame. From what portion of the molecule can methanol be produced? Write an equation for this reaction.

86. Glutathione, a tripeptide found in virtually all cells, functions as a reducing agent. The structure of glutathione is



What amino acids make up glutathione?

87. Draw the structures of the two dipeptides that can be formed from serine and alanine.

88. Draw the structures of the tripeptides gly-ala-ser and ser-ala-gly. How many other tripeptides are possible using these three amino acids?

89. Write the sequence of all possible tetrapeptides composed of the following amino acids.

a. Two phenylalanines and two glycines
b. Two phenylalanines, glycine, and alanine

90. How many different pentapeptides can be formed using five different amino acids?

91. Give an example of amino acids that could give rise to the interactions pictured in Fig. 22.24 that maintain the tertiary structures of proteins.

92. What types of interactions can occur between the side chains of the following amino acids that would help maintain the tertiary structure of a protein?

a. cysteine and cysteine c. glutamic acid and lysine
b. glutamine and serine d. proline and leucine

93. Oxygen is carried from the lungs to tissues by the protein hemoglobin in red blood cells. Sick cell anemia is a disease

resulting from abnormal hemoglobin molecules in which a valine is substituted for a single glutamic acid in normal hemoglobin. How might this substitution affect the structure of hemoglobin?

94. Over 100 different kinds of mutant hemoglobin molecules have been detected in humans. Unlike sickle cell anemia (see Exercise 93), not all of these mutations are as serious. In one nonlethal mutation, glutamine substitutes for a single glutamic acid in normal hemoglobin. Rationalize why this substitution is nonlethal.

95. Draw cyclic structures for D-ribose and D-mannose.

96. Indicate the chiral carbon atoms found in the monosaccharides D-ribose and D-mannose.

97. In addition to using *numerical* prefixes in the general names of sugars to indicate how many carbon atoms are present, we often use the prefixes *keto-* and *aldo-* to indicate whether the sugar is a ketone or an aldehyde. For example, the monosaccharide fructose is frequently called a *keto*hexose to emphasize that it contains six carbons as well as the ketone functional group. For each of the monosaccharides shown in Table 22.8 classify the sugars as aldohexoses, aldopentoses, ketohexoses, or ketopentoses.

98. Glucose can occur in three forms: two cyclic forms and one open-chain structure. In aqueous solution, only a tiny fraction of the glucose is in the open-chain form. Yet tests for the presence of glucose depend on reaction with the aldehyde group, which is found only in the open-chain form. Explain why these tests work.

99. What are the structural differences between α - and β -glucose? These two cyclic forms of glucose are the building blocks to form two different polymers. Explain.

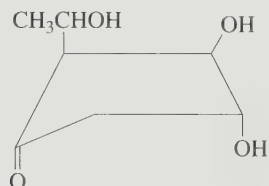
100. Cows can digest cellulose, but humans can't. Why not?

101. Which of the amino acids in Fig. 22.18 contain more than one chiral carbon atom? Draw the structures of these amino acids and indicate all chiral carbon atoms.

102. Why is glycine not optically active?

103. Which of the noncyclic isomers of bromochloropropene are optically active?

104. How many chiral carbon atoms does the following structure have?



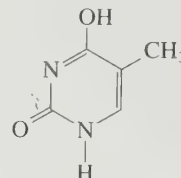
105. Part of a certain DNA sequence is G-G-T-C-T-A-T-A-C. What is the complementary sequence?

106. The codons (words) in DNA (that specify which amino acid should be at a particular point in a protein) are three bases

long. How many such three-letter words can be made from the four bases adenine, cytosine, guanine, and thymine?

107. Which base will hydrogen bond with uracil within an RNA molecule? Draw the structure of this base pair.

108. Tautomers are molecules that differ in the position of a hydrogen atom. A tautomeric form of thymine has the structure



If the tautomer above, rather than the stable form of thymine were present in a strand of DNA during replication, what would be the result?

109. The base sequences in mRNA that code for certain amino acids are

Glu: GAA, GAG
Val: GUU, GUC, GUA, GUG
Met: AUG
Trp: UGG
Phe: UUU, UUC
Asp: GAU, GAC

These sequences are complementary to the sequences in DNA.

- Give the corresponding sequences in DNA for the amino acids listed above.
 - Give a DNA sequence that would code for the peptide trp-glu-phe-met.
 - How many different DNA sequences can code for the butapeptide in part b?
 - What is the peptide that is produced from the DNA sequence T-A-C-C-T-G-A-A-G?
 - What other DNA sequences would yield the same tripeptide as in part d?
110. The change of a single base in the DNA sequence for normal hemoglobin can encode for the abnormal hemoglobin giving rise to sickle cell anemia. Which base in the codon for glu in DNA is replaced to give the codon(s) for val? (See Exercises 93 and 109.)

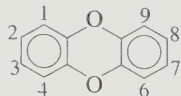
Additional Exercises

111. There is only one compound that is named 1,2-dichloroethane, but there are two distinct compounds that can be named 1,2-dichloroethene. Why?

112. In the presence of light, chlorine can substitute for one (or more) of the hydrogens in an alkane. For the following reactions, draw the possible monochlorination products.

- 2,2-dimethylpropane + $\text{Cl}_2 \xrightarrow{h\nu}$
- 1,3-dimethylcyclobutane + $\text{Cl}_2 \xrightarrow{h\nu}$
- 2,3-dimethylbutane + $\text{Cl}_2 \xrightarrow{h\nu}$

- 113.** Polychlorinated dibenzo-*p*-dioxins (PCDDs) are highly toxic substances that are present in trace amounts as by-products of some chemical manufacturing processes. They have been implicated in a number of environmental incidents—for example, the chemical contamination at Love Canal and the herbicide spraying in Vietnam. The structure of dibenzo-*p*-dioxin, along with the customary numbering convention, is:



The most toxic PCDD is 2,3,7,8-tetrachloro-dibenzo-*p*-dioxin. Draw the structure of this compound. Also draw the structures of two other isomers containing four chlorine atoms.

- 114.** Draw the isomer(s) specified. There may be more than one possible isomer for each part.

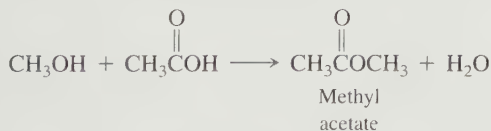
- a cyclic compound that is an isomer of *trans*-2 butene
- an ester that is an isomer of propanoic acid
- a ketone that is an isomer of butanal
- a secondary amine that is an isomer of butylamine
- a tertiary amine that is an isomer of butylamine
- an ether that is an isomer of 2-methyl-2-propanol
- a secondary alcohol that is an isomer of 2-methyl-2-propanol

- 115.** Explain why methyl alcohol is soluble in water in all proportions, while stearyl alcohol [$\text{CH}_3(\text{CH}_2)_{16}\text{OH}$] is a waxy solid that is not soluble in water.

- 116.** Is octanoic acid more soluble in 1 *M* HCl, 1 *M* NaOH, or pure water? Explain. Drugs such as morphine ($\text{C}_{17}\text{H}_{19}\text{NO}_3$) are often treated with strong acids. The most commonly used form of morphine is morphine hydrochloride ($\text{C}_{17}\text{H}_{20}\text{ClNO}_3$). Why is morphine treated in this way? (*Hint:* Morphine is an amine.)

- 117.** Consider the compounds butanoic acid, pentanal, *n*-hexane, and 1-pentanol. The boiling points of these compounds (in no specific order) are 69°C, 103°C, 137°C, and 164°C. Match the boiling points to the correct compound.

- 118.** Consider the reaction to produce the ester methyl acetate:



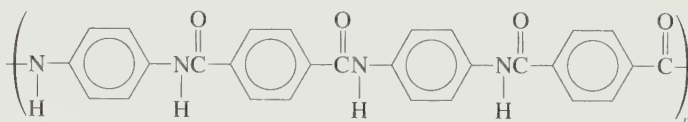
When this reaction is carried out with CH_3OH containing radioactive oxygen-18, the water produced does not contain oxygen-18. Explain the results of this radioisotope tracer experiment.

- 119.** A compound containing only carbon and hydrogen is 85.63% C by mass. Reaction of this compound with H_2O produces a secondary alcohol as the major product and a primary alcohol as the minor product (see Exercise 62). If the molar mass of the hydrocarbon is between 50 and 60 g/mol, name the compound.

- 120.** The polymer nitrile is a copolymer made from acrylonitrile and butadiene; it is used to make automotive hoses and gas-kets. Draw the structure of nitrile. (*Hint:* See Table 22.7.)

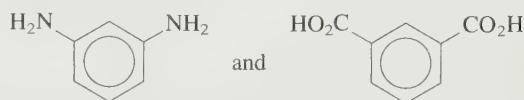
- 121.** *Polyaramid* is a term applied to polyamides containing aromatic groups. These polymers were originally made for use as tire cords but have since found many other uses.

- a.** Kevlar is used in bulletproof vests and many high-strength composites. The structure of Kevlar is



Which monomers are used to make Kevlar?

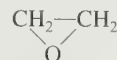
- b.** Nomex is a polyaramid used in fire-resistant clothing. It is a copolymer of



Draw the structure of the Nomex polymer. How do Kevlar and Nomex differ in their structures?

- 122.** When acrylic polymers are burned, toxic fumes are produced. For example, in many airplane fires, more passenger deaths have been caused by breathing toxic fumes than by the fire itself. Using polyacrylonitrile as an example, what would you expect to be one of the most toxic, gaseous combustion products created in the reaction?

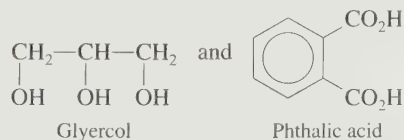
- 123.** Ethylene oxide,



is an important industrial chemical. Although most ethers are unreactive, ethylene oxide is quite reactive. It resembles C_2H_4 in its reactions in that addition reactions occur across the C—O bond in ethylene oxide.

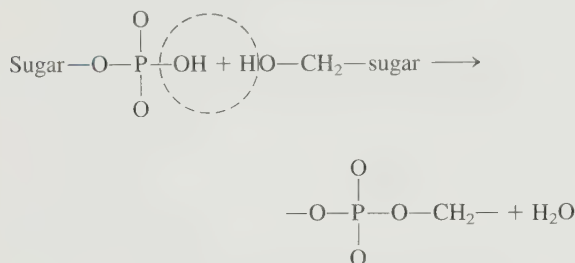
- Why is ethylene oxide so reactive? (*Hint:* Consider the bond angles in ethylene oxide as compared with those predicted by the VSEPR model.)
- Ethylene oxide undergoes addition polymerization, forming a polymer used in many applications requiring a non-ionic surfactant. Draw the structure of this polymer.

- 124.** Another way of producing highly crosslinked polyesters is to use glycerol. Alkyd resins are a polymer of this type. The polymer forms very tough coatings when baked onto a surface and is used in paints for automobiles and large appliances. Draw the structure of the polymer formed from the condensation of



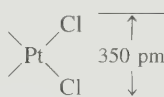
Explain how crosslinking occurs in this polymer.

125. Monosodium glutamate (MSG) is commonly used as a flavoring in foods. Draw the structure of MSG.
126. a. Use bond energies (Table 8.4) to estimate ΔH for the reaction of two molecules of glycine to form a peptide linkage.
b. Would you predict ΔS to favor the formation of peptide linkages between two molecules of glycine?
c. Would you predict the formation of proteins to be a spontaneous process?
127. The reaction to form a phosphate ester linkage between two nucleotides can be approximated as follows:



Would you predict the formation of a dinucleotide from two nucleotides to be a spontaneous process?

128. Considering your answers to Exercises 126 and 127, how can you justify the existence of proteins and nucleic acids in light of the second law of thermodynamics?
129. All amino acids have at least two functional groups with acidic or basic properties. In alanine, the carboxylic acid group has $K_a = 4.5 \times 10^{-3}$ and the amino group has $K_b = 7.4 \times 10^{-5}$. Three ions of alanine are possible when alanine is dissolved in water. Which of these ions would predominate in a solution with $[\text{H}^+] = 1.0 \text{ M}$? In a solution with $[\text{OH}^-] = 1.0 \text{ M}$?
130. The average molar mass of one base pair of nucleotides in DNA is approximately 600 g/mol. The spacing between successive base pairs is about 0.34 nm, and a complete turn in the helical structure of DNA occurs about every 3.4 nm. If a DNA molecule has a molar mass of $4.5 \times 10^9 \text{ g/mol}$, approximately how many complete turns exist in the DNA α -helix structure?
131. The compound cisplatin appears to kill cancer cells by inhibiting DNA synthesis. Given the following structural information about cisplatin, the information in Exercise 130, and the fact that the chloride ion is easily displaced by other donor molecules in cisplatin, speculate on how cisplatin may interact with DNA.



132. In glycine, the carboxylic acid group has $K_a = 4.3 \times 10^{-3}$ and the amino group has $K_b = 6.0 \times 10^{-5}$. Use these equilibrium constant values to calculate the equilibrium constants for the following.

- a. $^+\text{H}_3\text{NCH}_2\text{CO}_2^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{NCH}_2\text{CO}_2^- + \text{H}_3\text{O}^+$
b. $\text{H}_2\text{NCH}_2\text{CO}_2^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{NCH}_2\text{CO}_2\text{H} + \text{OH}^-$
c. $^+\text{H}_3\text{NCH}_2\text{CO}_2\text{H} \rightleftharpoons 2\text{H}^+ + \text{H}_2\text{NCH}_2\text{CO}_2^-$

Challenge Problems

133. The isoelectric point of an amino acid is the pH at which the molecule has no net charge. For glycine, that point would be the pH at which virtually all glycine molecules are in the form $^+\text{H}_3\text{NCH}_2\text{CO}_2^-$. This form of glycine is amphoteric since it can act as both an acid and a base. If we assume that the principal equilibrium at the isoelectric point has the best acid reacting with the best base present, then the reaction is

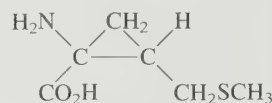


Assuming this reaction is the principal equilibrium, then the following relationship must hold true:

$$[\text{H}_2\text{NCH}_2\text{CO}_2^-] = [^+\text{H}_3\text{NCH}_2\text{CO}_2\text{H}] \quad (\text{ii})$$

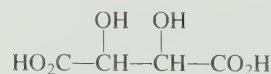
Use this result and your answer to part c of Exercise 132 to calculate the pH at which equation (ii) is true. It will be the isoelectric point of glycine.

134. In 1994 chemists at Texas A & M University reported the synthesis of a non-naturally occurring amino acid (*C & E News*, April 18, 1994, pp. 26–27):

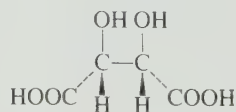


- a. To which naturally occurring amino acid is this compound most similar?
b. A tetrapeptide, phe-met-arg-phe-NH₂, is synthesized in the brains of rats addicted to morphine and heroin. (The —NH₂ indicates that the peptide ends in —C(=O)—NH₂ instead of —CO₂H.) The TAMU scientists synthesized a similar tetrapeptide, with the synthetic amino acid above replacing one of the original amino acids. Draw a structure for the tetrapeptide containing the synthetic amino acid.
c. Indicate the chiral carbon atoms in the synthetic amino acid.

135. The structure of tartaric acid is



- a. Is the form of tartaric acid pictured below optically active? Explain.



Note: The dashed lines show groups behind the plane of the page. The wedges show groups in front of the plane.

b. Draw the optically active forms of tartaric acid.

136. Using one of the Lewis structures for benzene (C_6H_6), estimate ΔH_f° for $C_6H_6(g)$ using bond energies and given the standard enthalpy of formation of $C(g)$ is 717 kJ/mol. The experimental ΔH_f° value for $C_6H_6(g)$ is 83 kJ/mol. Explain the discrepancy between the experimental value and the calculated ΔH_f° value for $C_6H_6(g)$.

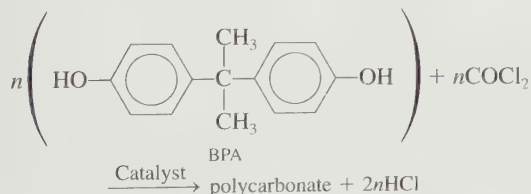
137. Mycomycin, a naturally occurring antibiotic produced by the fungus *Nocardia acidophilus*, has the molecular formula $C_{13}H_{10}O_2$ and the systematic name 3,5,7,8-tridecatetraene-10,12-diyonic acid. Draw the structure of mycomycin.

138. Sorbic acid is used to prevent mold and fungus growth in some food products, especially cheeses. The systematic name for sorbic acid is 2,4-hexadienoic acid. Draw structures for the four geometrical isomers of sorbic acid.

139. Consider the following reactions. For parts b–d, see Exercise 62.

- When C_5H_{12} is reacted with $Cl_2(g)$ in the presence of ultraviolet light, four different monochlorination products form. What is the structure of C_5H_{12} in this reaction?
- When C_4H_8 is reacted with H_2O , a tertiary alcohol is produced as the major product. What is the structure of C_4H_8 in this reaction?
- When C_7H_{12} is reacted with HCl , 1-chloro-1-methylcyclohexane is produced as the major product. What are the two possible structures for C_7H_{12} in this reaction?
- When a hydrocarbon is reacted with H_2O and the major product of this reaction is then oxidized, acetone (2-propanone) is produced. What is the structure of the hydrocarbon in this reaction?
- When $C_5H_{12}O$ is oxidized, a carboxylic acid is produced. What are the possible structures for $C_5H_{12}O$ in this reaction?

140. Polycarbonates are a class of thermoplastic polymers that are used in the plastic lenses of eyeglasses and in the shells of bicycle helmets. A polycarbonate is made from the reaction of bisphenol A (BPA) with phosgene ($COCl_2$):

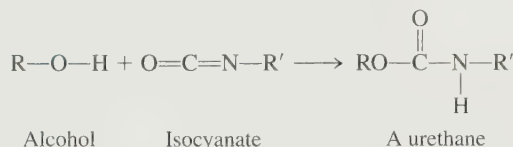


Phenol (C_6H_5OH) is used to terminate the polymer (stop its growth).

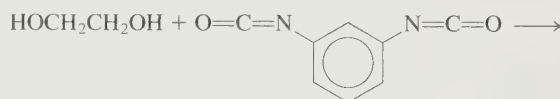
- a. Draw the structure of the polycarbonate chain formed from the above reaction.

- b. Is this reaction a condensation or addition polymerization?

141. A urethane linkage occurs when an alcohol adds across the carbon–nitrogen double bond in an isocyanate:



Polyurethanes (formed from the copolymerization of a diol with a diisocyanate) are used in foamed insulation and a variety of other construction materials. What is the structure of the polyurethane formed by the following reaction?



142. ABS plastic is a tough, hard plastic used in applications requiring shock resistance. The polymer consists of three monomer units: acrylonitrile (C_3H_3N), butadiene (C_4H_6), and styrene (C_8H_8).

- Draw two repeating units of ABS plastic assuming that the three monomer units react in a 1:1:1 mole ratio and react in the same order as the monomers listed above.
- A sample of ABS plastic contains 8.80% N by mass. It took 0.605 g of Br_2 to react completely with a 1.20-g sample of ABS plastic. What is the percent by mass of acrylonitrile, butadiene, and styrene in this polymer sample?
- ABS plastic does not react in a 1:1:1 mole ratio among the three monomer units. Using the results from part b, determine the relative numbers of the monomer units in this sample of ABS plastic.

143. Stretch a rubber band while holding it gently to your lips. Then slowly let it relax while still in contact with your lips.

- What happens to the temperature of the rubber band on stretching?
- Is the stretching an exothermic or endothermic process?
- Explain the above result in terms of intermolecular forces.
- What is the sign of ΔS and ΔG for stretching the rubber band?
- Give the molecular explanation for the sign of ΔS for stretching.

144. Read the label on an over-the-counter medication (Tylenol, cough syrup, etc.) or cosmetic. Look up the structures of the organic compounds listed in a reference such as *The Merck Index*. From the information given, determine the function of each of the compounds you looked up.

 Media Activities

1. Open the Synthesis of Nylon Visualization on the student CD. What type of polymer is nylon? Nylon is a copolymer. What does this mean? Review Figure 22.16 in the text for the structures of the monomers useful to produce the nylon in the video. What small molecule is eliminated when the nylon in the video forms? For more practice with condensation polymers, do Exercises 22.75 and 22.77 in the text.
2. Explain why carbohydrates are also polymers. Open the Molecule Library on the student web site and view D-fructose and D-glucose to see two different monosaccharides.
3. Sucrose is a disaccharide. What does this mean and what two monosaccharides form sucrose? Open the Molecule Library on the student web site and view sucrose. Starch, cellulose, and glycogen are polysaccharides. What does this mean? What monomer is used to produce starch, cellulose, and glycogen?
4. DNA and RNA are also polymers. However, the monomers used to form these polymers are more complicated than in proteins and carbohydrates. For DNA and RNA, each monomer contains three parts. What are the three parts? Open the Mol-

ecule Library on the student web site and view the sugar part (deoxyribose in DNA and ribose in RNA) and the nitrogen-containing base part (uracil, cytosine, thymine, adenine, and guanine). What are the base pairs in the DNA double-helix structure?

5. Lipids are a class of substances that are water insoluble; they contain mostly carbon and hydrogen atoms. Does this make sense in view of the lipids inability to dissolve in water? Fats are one type of lipid. Open the Molecule Library on the student web site and view tristearin, the most common animal fat. Tristearin is a triglyceride.
6. Steroids are another type of lipid. Open the Molecule Library on the student web site and view the steroids cholesterol, testosterone, progesterone, estradiol, and cholic acid. What common structural characteristic do all steroids have?
7. Test your understanding of Chapter 22 material by taking the ACE quizzes on the student web site.



For additional web activities and other resources, visit the Zumdahl, *Chemistry*, Sixth Edition textbook site at <http://chemistry.college.hmco.com/students>.

Appendixes

Appendix One Mathematical Procedures

A1.1 Exponential Notation

The numbers characteristic of scientific measurements are often very large or very small; thus it is convenient to express them using powers of 10. For example, the number 1,300,000 can be expressed as 1.3×10^6 , which means multiply 1.3 by 10 six times, or

$$1.3 \times 10^6 = 1.3 \times \underbrace{10 \times 10 \times 10 \times 10 \times 10 \times 10}_{10^6 = 1 \text{ million}}$$

Note that each multiplication by 10 moves the decimal point one place to the right:

$$\begin{aligned} 1.3 \times 10 &= 13. \\ 13 \times 10 &= 130. \\ 130 \times 10 &= 1300. \\ &\vdots \end{aligned}$$

Thus the easiest way to interpret the notation 1.3×10^6 is that it means move the decimal point in 1.3 to the right six times:

$$1.3 \times 10^6 = \underbrace{1\ 3\ 0\ 0\ 0\ 0\ 0}_{1\ 2\ 3\ 4\ 5\ 6} = 1,300,000$$

Using this notation, the number 1985 can be expressed as 1.985×10^3 . Note that the usual convention is to write the number that appears before the power of 10 as a number between 1 and 10. To end up with the number 1.985, which is between 1 and 10, we had to move the decimal point three places to the left. To compensate for that, we must multiply by 10^3 , which says that to get the intended number we start with 1.985 and move the decimal point three places to the right; that is:

$$1.985 \times 10^3 = \underbrace{1\ 9\ 8\ 5.}_{1\ 2\ 3}$$

Some other examples are given below.

Number	Exponential Notation
5.6	5.6×10^0 or 5.6×1
39	3.9×10^1
943	9.43×10^2
1126	1.126×10^3

So far we have considered numbers greater than 1. How do we represent a number such as 0.0034 in exponential notation? We start with a number between 1 and 10 and *divide* by the appropriate power of 10:

$$0.0034 = \frac{3.4}{10 \times 10 \times 10} = \frac{3.4}{10^3} = 3.4 \times 10^{-3}$$

Division by 10 moves the decimal point one place to the *left*. Thus the number



can be written as 1.4×10^{-7} .

To summarize, we can write any number in the form

$$N \times 10^{\pm n}$$

where N is between 1 and 10 and the exponent n is an integer. If the sign preceding n is positive, it means the decimal point in N should be moved n places to the right. If a negative sign precedes n , the decimal point in N should be moved n places to the left.

Multiplication and Division

When two numbers expressed in exponential notation are multiplied, the initial numbers are multiplied and the exponents of 10 are added:

$$(M \times 10^m)(N \times 10^n) = (MN) \times 10^{m+n}$$

For example (to two significant figures, as required),

$$(3.2 \times 10^4)(2.8 \times 10^3) = 9.0 \times 10^7$$

When the numbers are multiplied, if a result greater than 10 is obtained for the initial number, the decimal point is moved one place to the left and the exponent of 10 is increased by 1:

$$\begin{aligned} (5.8 \times 10^2)(4.3 \times 10^8) &= 24.9 \times 10^{10} \\ &= 2.49 \times 10^{11} \\ &= 2.5 \times 10^{11} \quad (\text{two significant figures}) \end{aligned}$$

Division of two numbers expressed in exponential notation involves normal division of the initial numbers and *subtraction* of the exponent of the divisor from that of the dividend. For example,

$$\frac{4.8 \times 10^8}{2.1 \times 10^3} = \frac{4.8}{2.1} \times 10^{(8-3)} = 2.3 \times 10^5$$

Divisor

If the initial number resulting from the division is less than 1, the decimal point is moved one place to the right and the exponent of 10 is decreased by 1. For example,

$$\begin{aligned} \frac{6.4 \times 10^3}{8.3 \times 10^5} &= \frac{6.4}{8.3} \times 10^{(3-5)} = 0.77 \times 10^{-2} \\ &= 7.7 \times 10^{-3} \end{aligned}$$

Addition and Subtraction

To add or subtract numbers expressed in exponential notation, *the exponents of the numbers must be the same*. For example, to add 1.31×10^5 and 4.2×10^4 , we must rewrite one number so that the exponents of both are the same. The number

1.31×10^5 can be written 13.1×10^4 , since moving the decimal point one place to the right can be compensated for by decreasing the exponent by 1. Now we can add the numbers:

$$\begin{array}{r} 13.1 \times 10^4 \\ + 4.2 \times 10^4 \\ \hline 17.3 \times 10^4 \end{array}$$

In correct exponential notation the result is expressed as 1.73×10^5 .

To perform addition or subtraction with numbers expressed in exponential notation, only the initial numbers are added or subtracted. The exponent of the result is the same as those of the numbers being added or subtracted. To subtract 1.8×10^2 from 8.99×10^3 , we write

$$\begin{array}{r} 8.99 \times 10^3 \\ - 0.18 \times 10^3 \\ \hline 8.81 \times 10^3 \end{array}$$

Powers and Roots

When a number expressed in exponential notation is taken to some power, the initial number is taken to the appropriate power and the exponent of 10 is multiplied by that power:

$$(N \times 10^n)^m = N^m \times 10^{m \cdot n}$$

For example,*

$$\begin{aligned} (7.5 \times 10^2)^3 &= 7.5^3 \times 10^{3 \cdot 2} \\ &= 422 \times 10^6 \\ &= 4.22 \times 10^8 \\ &= 4.2 \times 10^8 \quad (\text{two significant figures}) \end{aligned}$$

When a root is taken of a number expressed in exponential notation, the root of the initial number is taken and the exponent of 10 is divided by the number representing the root:

$$\sqrt[n]{N \times 10^n} = (n \times 10^n)^{1/2} = \sqrt{N} \times 10^{n/2}$$

For example,

$$\begin{aligned} (2.9 \times 10^6)^{1/2} &= \sqrt{2.9} \times 10^{6/2} \\ &= 1.7 \times 10^3 \end{aligned}$$

Because the exponent of the result must be an integer, we may sometimes have to change the form of the number so that the power divided by the root equals an integer. For example,

$$\begin{aligned} \sqrt{1.9 \times 10^3} &= (1.9 \times 10^3)^{1/2} = (0.19 \times 10^4)^{1/2} \\ &= \sqrt{0.19} \times 10^2 \\ &= 0.44 \times 10^2 \\ &= 4.4 \times 10^1 \end{aligned}$$

*Refer to the instruction booklet for your calculator for directions concerning how to take roots and powers of numbers.

In this case, we moved the decimal point one place to the left and increased the exponent from 3 to 4 to make $n/2$ an integer.

The same procedure is followed for roots other than square roots. For example,

$$\begin{aligned}\sqrt[3]{6.9 \times 10^5} &= (6.9 \times 10^5)^{1/3} = (0.69 \times 10^6)^{1/3} \\ &= \sqrt[3]{0.69} \times 10^2 \\ &= 0.88 \times 10^2 \\ &= 8.8 \times 10^1\end{aligned}$$

and

$$\begin{aligned}\sqrt[3]{4.6 \times 10^{10}} &= (4.6 \times 10^{10})^{1/3} = (46 \times 10^9)^{1/3} \\ &= \sqrt[3]{46} \times 10^3 \\ &= 3.6 \times 10^3\end{aligned}$$

A1.2 Logarithms

A logarithm is an exponent. Any number N can be expressed as follows:

$$N = 10^x$$

For example,

$$\begin{aligned}1000 &= 10^3 \\ 100 &= 10^2 \\ 10 &= 10^1 \\ 1 &= 10^0\end{aligned}$$

The common, or base 10, logarithm of a number is the power to which 10 must be taken to yield the number. Thus, since $1000 = 10^3$,

$$\log 1000 = 3$$

Similarly,

$$\begin{aligned}\log 100 &= 2 \\ \log 10 &= 1 \\ \log 1 &= 0\end{aligned}$$

For a number between 10 and 100, the required exponent of 10 will be between 1 and 2. For example, $65 = 10^{1.8129}$; that is, $\log 65 = 1.8129$. For a number between 100 and 1000, the exponent of 10 will be between 2 and 3. For example, $650 = 10^{2.8129}$ and $\log 650 = 2.8129$.

A number N greater than 0 and less than 1 can be expressed as follows:

$$N = 10^{-x} = \frac{1}{10^x}$$

For example,

$$\begin{aligned}0.001 &= \frac{1}{1000} = \frac{1}{10^3} = 10^{-3} \\ 0.01 &= \frac{1}{100} = \frac{1}{10^2} = 10^{-2} \\ 0.1 &= \frac{1}{10} = \frac{1}{10^1} = 10^{-1}\end{aligned}$$

Thus

$$\log 0.001 = -3$$

$$\log 0.01 = -2$$

$$\log 0.1 = -1$$

Although common logs are often tabulated, the most convenient method for obtaining such logs is to use an electronic calculator. On most calculators the number is first entered and then the log key is punched. The log of the number then appears in the display.* Some examples are given below. You should reproduce these results on your calculator to be sure that you can find common logs correctly.

Number	Common Log
36	1.56
1849	3.2669
0.156	-0.807
1.68×10^{-5}	-4.775

Note that the number of digits after the decimal point in a common log is equal to the number of significant figures in the original number.

Since logs are simply exponents, they are manipulated according to the rules for exponents. For example, if $A = 10^x$ and $B = 10^y$, then their product is

$$A \cdot B = 10^x \cdot 10^y = 10^{x+y}$$

and

$$\log AB = x + y = \log A + \log B$$

For division, we have

$$\frac{A}{B} = \frac{10^x}{10^y} = 10^{x-y}$$

and

$$\log \frac{A}{B} = x - y = \log A - \log B$$

For a number raised to a power, we have

$$A^n = (10^x)^n = 10^{nx}$$

and

$$\log A^n = nx = n \log A$$

It follows that

$$\log \frac{1}{A^n} = \log A^{-n} = -n \log A$$

or, for $n = 1$,

$$\log \frac{1}{A} = -\log A$$

*Refer to the instruction booklet for your calculator for the exact sequence to obtain logarithms.

When a common log is given, to find the number it represents, we must carry out the process of exponentiation. For example, if the log is 2.673, then $N = 10^{2.673}$. The process of exponentiation is also called taking the antilog, or the inverse logarithm. This operation is usually carried out on calculators in one of two ways. The majority of calculators require that the log be entered first and then the keys $\boxed{\text{INV}}$ and $\boxed{\text{LOG}}$ pressed in succession. For example, to find $N = 10^{2.673}$ we enter 2.673 and then press $\boxed{\text{INV}}$ and $\boxed{\text{LOG}}$. The number 471 will be displayed; that is, $N = 471$. Some calculators have a $\boxed{10^x}$ key. In that case, the log is entered first and then the $\boxed{10^x}$ key is pressed. Again, the number 471 will be displayed.

Natural logarithms, another type of logarithm, are based on the number 2.7183, which is referred to as e . In this case, a number is represented as $N = e^x = 2.7183^x$. For example,

$$N = 7.15 = e^x$$

$$\ln 7.15 = x = 1.967$$

To find the natural log of a number using a calculator, the number is entered and then the $\boxed{\ln}$ key is pressed. Use the following examples to check your technique for finding natural logs with your calculator:

Number (e^x)	Natural Log(x)
784	6.664
1.61×10^3	7.384
1.00×10^{-7}	-16.118
1.00	0

If a natural logarithm is given, to find the number it represents, exponentiation to the base e (2.7183) must be carried out. With many calculators this is done using a key marked $\boxed{e^x}$ (the natural log is entered, with the correct sign, and then the $\boxed{e^x}$ key is pressed). The other common method for exponentiation to base e is to enter the natural log and then press the $\boxed{\text{INV}}$ and $\boxed{\ln}$ keys in succession. The following examples will help you check your technique:

$\ln N(x)$	$N(e^x)$
3.256	25.9
-5.169	5.69×10^{-3}
13.112	4.95×10^5

Since natural logarithms are simply exponents, they are also manipulated according to the mathematical rules for exponents given above for common logs.

A1.3 Graphing Functions

In interpreting the results of a scientific experiment, it is often useful to make a graph. If possible, the function to be graphed should be in a form that gives a straight line. The equation for a straight line (a *linear equation*) can be represented by the general form

$$y = mx + b$$

where y is the *dependent variable*, x is the *independent variable*, m is the *slope*, and b is the *intercept* with the y axis.

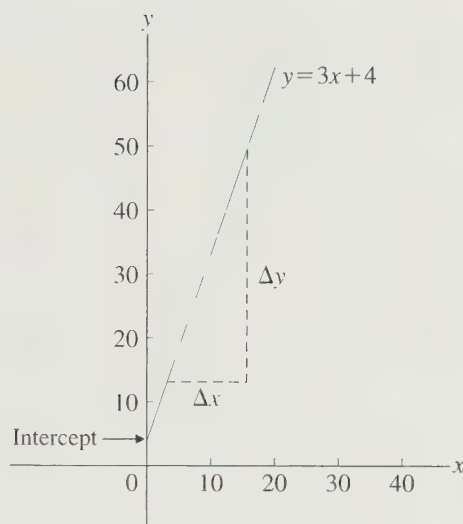


FIGURE A.1
Graph of the linear equation
 $y = 3x + 4$.

To illustrate the characteristics of a linear equation, the function $y = 3x + 4$ is plotted in Fig. A.1. For this equation $m = 3$ and $b = 4$. Note that the y intercept occurs when $x = 0$. In this case the intercept is 4, as can be seen from the equation ($b = 4$).

The slope of a straight line is defined as the ratio of the rate of change in y to that in x :

$$m = \text{slope} = \frac{\Delta y}{\Delta x}$$

For the equation $y = 3x + 4$, y changes three times as fast as x (since x has a coefficient of 3). Thus the slope in this case is 3. This can be verified from the graph. For the triangle shown in Fig. A.1,

$$\Delta y = 34 - 10 = 24 \quad \text{and} \quad \Delta x = 10 - 2 = 8$$

Thus

$$\text{Slope} = \frac{\Delta y}{\Delta x} = \frac{24}{8} = 3$$

The preceding example illustrates a general method for obtaining the slope of a line from the graph of that line. Simply draw a triangle with one side parallel to the y axis and the other parallel to the x axis as shown in Fig. A.1. Then determine the lengths of the sides to give Δy and Δx , respectively, and compute the ratio $\Delta y/\Delta x$.

Sometimes an equation that is not in standard form can be changed to the form $y = mx + b$ by rearrangement or mathematical manipulation. An example is the equation $k = Ae^{-E_a/RT}$ described in Section 12.7, where A , E_a , and R are constants; k is the dependent variable; and $1/T$ is the independent variable. This equation can be changed to standard form by taking the natural logarithm of both sides,

$$\ln k = \ln Ae^{-E_a/RT} = \ln A + \ln e^{-E_a/RT} = \ln A - \frac{E_a}{RT}$$

noting that the log of a product is equal to the sum of the logs of the individual terms and that the natural log of $e^{-E_a/RT}$ is simply the exponent $-E_a/RT$. Thus, in

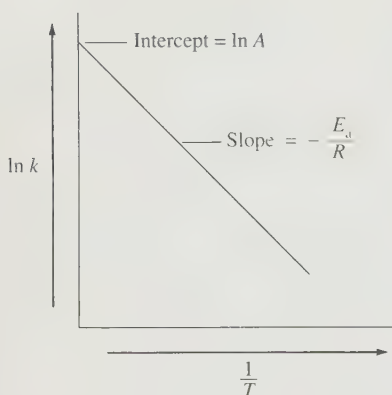


FIGURE A.2
Graph of $\ln k$ versus $1/T$.

TABLE A.1 Some Useful Linear Equations in Standard Form

Equation ($y = mx + b$)	What Is Plotted (y vs. x)	Slope (m)	Intercept (b)	Section in Text
$[A] = -kt + [A]_0$	$[A]$ vs. t	$-k$	$[A]_0$	12.4
$\ln[A] = -kt + \ln[A]_0$	$\ln[A]$ vs. t	$-k$	$\ln[A]_0$	12.4
$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$	$\frac{1}{[A]}$ vs. t	k	$\frac{1}{[A]_0}$	12.4
$\ln P_{\text{vap}} = -\frac{\Delta H_{\text{vap}}}{R}\left(\frac{1}{T}\right) + C$	$\ln P_{\text{vap}}$ vs. $\frac{1}{T}$	$-\frac{\Delta H_{\text{vap}}}{R}$	C	10.8

standard form, the equation $k = Ae^{-E_a/RT}$ is written

$$\underbrace{\ln k}_{\substack{\uparrow \\ y}} = \underbrace{-\frac{E_a}{R}}_{\substack{\uparrow \\ m}} \underbrace{\left(\frac{1}{T}\right)}_{\substack{\uparrow \\ x}} + \underbrace{\ln A}_{\substack{\uparrow \\ b}}$$

A plot of $\ln k$ versus $1/T$ (see Fig. A.2) gives a straight line with slope $-E_a/R$ and intercept $\ln A$.

Other linear equations that are useful in the study of chemistry are listed in standard form in Table A.1.

A1.4 Solving Quadratic Equations

A *quadratic equation*, a polynomial in which the highest power of x is 2, can be written as

$$ax^2 + bx + c = 0$$

One method for finding the two values of x that satisfy a quadratic equation is to use the *quadratic formula*:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

where a , b , and c are the coefficients of x^2 and x and the constant, respectively. For example, in determining $[\text{H}^+]$ in a solution of $1.0 \times 10^{-4} M$ acetic acid the following expression arises:

$$1.8 \times 10^{-5} = \frac{x^2}{1.0 \times 10^{-4} - x}$$

which yields

$$x^2 + (1.8 \times 10^{-5})x - 1.8 \times 10^{-9} = 0$$

where $a = 1$, $b = 1.8 \times 10^{-5}$, and $c = -1.8 \times 10^{-9}$. Using the quadratic formula, we have

$$\begin{aligned} x &= \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \\ &= \frac{-1.8 \times 10^{-5} \pm \sqrt{3.24 \times 10^{-10} - (4)(1)(-1.8 \times 10^{-9})}}{2(1)} \end{aligned}$$

$$\begin{aligned}
 &= \frac{-1.8 \times 10^{-5} \pm \sqrt{3.24 \times 10^{-10} + 7.2 \times 10^{-9}}}{2} \\
 &= \frac{-1.8 \times 10^{-5} \pm \sqrt{7.5 \times 10^{-9}}}{2} \\
 &= \frac{-1.8 \times 10^{-5} \pm 8.7 \times 10^{-5}}{2}
 \end{aligned}$$

Thus

$$x = \frac{6.9 \times 10^{-5}}{2} = 3.5 \times 10^{-5}$$

and

$$x = \frac{-10.5 \times 10^{-5}}{2} = -5.2 \times 10^{-5}$$

Note that there are two roots, as there always will be, for a polynomial in x^2 . In this case x represents a concentration of H^+ (see Section 14.3). Thus the positive root is the one that solves the problem, since a concentration cannot be a negative number.

A second method for solving quadratic equations is by *successive approximations*, a systematic method of trial and error. A value of x is guessed and substituted into the equation everywhere x (or x^2) appears, except for one place. For example, for the equation

$$x^2 + (1.8 \times 10^{-5})x - 1.8 \times 10^{-9} = 0$$

we might guess $x = 2 \times 10^{-5}$. Substituting that value into the equation gives

$$x^2 + (1.8 \times 10^{-5})(2 \times 10^{-5}) - 1.8 \times 10^{-9} = 0$$

or

$$x^2 = 1.8 \times 10^{-9} - 3.6 \times 10^{-10} = 1.4 \times 10^{-9}$$

Thus

$$x = 3.7 \times 10^{-5}$$

Note that the guessed value of $x(2 \times 10^{-5})$ is not the same as the value of x that is calculated (3.7×10^{-5}) after inserting the estimated value. This means that $x = 2 \times 10^{-5}$ is not the correct solution, and we must try another guess. We take the calculated value (3.7×10^{-5}) as our next guess:

$$\begin{aligned}
 x^2 + (1.8 \times 10^{-5})(3.7 \times 10^{-5}) - 1.8 \times 10^{-9} &= 0 \\
 x^2 &= 1.8 \times 10^{-9} - 6.7 \times 10^{-10} = 1.1 \times 10^{-9}
 \end{aligned}$$

Thus

$$x = 3.3 \times 10^{-5}$$

Now we compare the two values of x again:

$$\begin{aligned}
 \text{Guessed: } x &= 3.7 \times 10^{-5} \\
 \text{Calculated: } x &= 3.3 \times 10^{-5}
 \end{aligned}$$

These values are closer but not close enough. Next we try 3.3×10^{-5} as our guess:

$$\begin{aligned}
 x^2 + (1.8 \times 10^{-5})(3.3 \times 10^{-5}) - 1.8 \times 10^{-9} &= 0 \\
 x^2 &= 1.8 \times 10^{-9} - 5.9 \times 10^{-10} = 1.2 \times 10^{-9}
 \end{aligned}$$

Thus

$$x = 3.5 \times 10^{-5}$$

Again we compare:

$$\text{Guessed: } x = 3.3 \times 10^{-5}$$

$$\text{Calculated: } x = 3.5 \times 10^{-5}$$

Next we guess $x = 3.5 \times 10^{-5}$ to give

$$x^2 + (1.8 \times 10^{-5})(3.5 \times 10^{-5}) - 1.8 \times 10^{-9} = 0$$

$$x^2 = 1.8 \times 10^{-9} - 6.3 \times 10^{-10} = 1.2 \times 10^{-9}$$

Thus

$$x = 3.5 \times 10^{-5}$$

Now the guessed value and the calculated value are the same; we have found the correct solution. Note that this agrees with one of the roots found with the quadratic formula in the first method above.

To further illustrate the method of successive approximations, we will solve Sample Exercise 14.17 using this procedure. In solving for $[H^+]$ for $0.010\text{ M H}_2\text{SO}_4$, we obtain the following expression:

$$1.2 \times 10^{-2} = \frac{x(0.010 + x)}{0.010 - x}$$

which can be rearranged to give

$$x = (1.2 \times 10^{-2}) \left(\frac{0.010 - x}{0.010 + x} \right)$$

We will guess a value for x , substitute it into the right side of the equation, and then calculate a value for x . In guessing a value for x , we know it must be less than 0.010, since a larger value will make the calculated value for x negative and the guessed and calculated values will never match. We start by guessing $x = 0.005$.

The results of the successive approximations are shown in the following table:

Trial	Guessed Value for x	Calculated Value for x
1	0.0050	0.0040
2	0.0040	0.0051
3	0.00450	0.00455
4	0.00452	0.00453

Note that the first guess was close to the actual value and that there was oscillation between 0.004 and 0.005 for the guessed and calculated values. For trial 3, an average of these values was used as the guess, and this led rapidly to the correct value (0.0045 to the correct number of significant figures). Also, note that it is useful to carry extra digits until the correct value is obtained. That value can then be rounded off to the correct number of significant figures.

The method of successive approximations is especially useful for solving polynomials containing x to a power of 3 or higher. The procedure is the same as for quadratic equations: Substitute a guessed value for x into the equation for every x term but one, and then solve for x . Continue this process until the guessed and calculated values agree.

A1.5 Uncertainties in Measurements

Like all the physical sciences, chemistry is based on the results of measurements. Every measurement has an inherent uncertainty, so if we are to use the results of measurements to reach conclusions, we must be able to estimate the sizes of these uncertainties.

For example, the specification for a commercial 500-mg acetaminophen (the active painkiller in Tylenol) tablet is that each batch of tablets must contain 450 to 550 mg of acetaminophen per tablet. Suppose that chemical analysis gave the following results for a batch of acetaminophen tablets: 428 mg, 479 mg, 442 mg, and 435 mg. How can we use these results to decide if the batch of tablets meets the specification? Although the details of how to draw such conclusions from measured data are beyond the scope of this text, we will consider some aspects of how this is done. We will focus here on the types of experimental uncertainty, the expression of experimental results, and a simplified method for estimating experimental uncertainty when several types of measurement contribute to the final result.

Types of Experimental Error

There are two types of experimental uncertainty (error). A variety of names are applied to these types of errors:

Precision $\longleftrightarrow$ random error $\equiv$ indeterminate error

Accuracy $\longleftrightarrow$ systematic error $\equiv$ determinate error

The difference between the two types of error is well illustrated by the attempts to hit a target shown in Fig. 1.7 in Chapter 1.

Random error is associated with every measurement. To obtain the last significant figure for any measurement, we must always make an estimate. For example, we interpolate between the marks on a meter stick, a buret, or a balance. The precision of replicate measurements (repeated measurements of the same type) reflects the size of the random errors. Precision refers to the reproducibility of replicate measurements.

The accuracy of a measurement refers to how close it is to the true value. An inaccurate result occurs as a result of some flaw (systematic error) in the measurement: the presence of an interfering substance, incorrect calibration of an instrument, operator error, and so on. The goal of chemical analysis is to eliminate systematic error, but random errors can only be minimized. In practice, an experiment is almost always done to find an unknown value (the true value is not known—someone is trying to obtain that value by doing the experiment). In this case the precision of several replicate determinations is used to assess the accuracy of the result. The results of the replicate experiments are expressed as an average (which we assume is close to the true value) with an error limit that gives some indication of how close the average value may be to the true value. The error limit represents the uncertainty of the experimental result.

Expression of Experimental Results

If we perform several measurements, such as for the analysis for acetaminophen in painkiller tablets, the results should express two things: the average of the measurements and the size of the uncertainty.

There are two common ways of expressing an average: the mean and the median. The mean ($\bar{x}$) is the arithmetic average of the results, or

$$\text{Mean} = \bar{x} = \frac{\sum_{i=1}^n x_i}{n} = \frac{x_1 + x_2 + \cdots + x_n}{n}$$

where Σ means take the sum of the values. The mean is equal to the sum of all the measurements divided by the number of measurements. For the acetaminophen results given previously, the mean is

$$\bar{x} = \frac{428 + 479 + 442 + 435}{4} = 446 \text{ mg}$$

The median is the value that lies in the middle among the results. Half the measurements are above the median and half are below the median. For results of 465 mg, 485 mg, and 492 mg, the median is 485 mg. When there is an even number of results, the median is the average of the two middle results. For the acetaminophen results, the median is

$$\frac{442 + 435}{2} = 438 \text{ mg}$$

There are several advantages to using the median. If a small number of measurements is made, one value can greatly affect the mean. Consider the results for the analysis of acetaminophen: 428 mg, 479 mg, 442 mg, and 435 mg. The mean is 446 mg, which is larger than three of the four weights. The median is 438 mg, which lies near the three values that are relatively close to one another.

In addition to expressing an average value for a series of results, we must express the uncertainty. This usually means expressing either the precision of the measurements or the observed range of the measurements. The range of a series of measurements is defined by the smallest value and the largest value. For the analytical results on the acetaminophen tablets, the range is from 428 mg to 479 mg. Using this range, we can express the results by saying that the true value lies between 428 mg and 479 mg. That is, we can express the amount of acetaminophen in a typical tablet as 446 ± 33 mg, where the error limit is chosen to give the observed range (approximately).

The most common way to specify precision is by the standard deviation, s , which for a small number of measurements is given by the formula

$$s = \left[\frac{\sum_{i=1}^n (x_i - \bar{x})^2}{n - 1} \right]^{1/2}$$

where x_i is an individual result, $\bar{x}$ is the average (either mean or median), and n is the total number of measurements. For the acetaminophen example, we have

$$s = \left[\frac{(428 - 446)^2 + (479 - 446)^2 + (442 - 446)^2 + (435 - 446)^2}{4 - 1} \right]^{1/2} = 23$$

Thus we can say the amount of acetaminophen in the typical tablet in the batch of tablets is 446 mg with a sample standard deviation of 23 mg. Statistically this means that any additional measurement has a 68% probability (68 chances out of 100) of being between 423 mg ($446 - 23$) and 469 mg ($446 + 23$). Thus the standard deviation is a measure of the precision of a given type of determination.

The standard deviation gives us a means of describing the precision of a given type of determination using a series of replicate results. However, it is also useful to be able to estimate the precision of a procedure that involves several measurements by combining the precisions of the individual steps. That is, we want to answer

the following question: How do the uncertainties propagate when we combine the results of several different types of measurements? There are many ways to deal with the propagation of uncertainty. We will discuss only one simple method here.

A Simplified Method for Estimating Experimental Uncertainty

To illustrate this method, we will consider the determination of the density of an irregularly shaped solid. In this determination we make three measurements. First, we measure the mass of the object on a balance. Next, we must obtain the volume of the solid. The easiest method for doing this is to partially fill a graduated cylinder with a liquid and record the volume. Then we add the solid and record the volume again. The difference in the measured volumes is the volume of the solid. We can then calculate the density of the solid from the equation

$$D = \frac{M}{V_2 - V_1}$$

where M is the mass of the solid, V_1 is the initial volume of liquid in the graduated cylinder, and V_2 is the volume of liquid plus solid. Suppose we get the following results:

$$M = 23.06 \text{ g}$$

$$V_1 = 10.4 \text{ mL}$$

$$V_2 = 13.5 \text{ mL}$$

The calculated density is

$$\frac{23.06 \text{ g}}{13.5 \text{ mL} - 10.4 \text{ mL}} = 7.44 \text{ g/mL}$$

Now suppose that the precision of the balance used is $\pm 0.02 \text{ g}$ and that the volume measurements are precise to $\pm 0.05 \text{ mL}$. How do we estimate the uncertainty of the density? We can do this by assuming a worst case. That is, we assume the largest uncertainties in all measurements, and see what combinations of measurements will give the largest and smallest possible results (the greatest range). Since the density is the mass divided by the volume, the largest value of the density will be that obtained using the largest possible mass and the smallest possible volume:

$$D_{\max} = \frac{\text{Largest possible mass} = 23.06 + .02}{\text{Smallest possible } V_2 \quad \text{Largest possible } V_1} = \frac{23.08}{13.45 - 10.45} = 7.69 \text{ g/mL}$$

The smallest value of the density is

$$D_{\min} = \frac{\text{Smallest possible mass} = 23.04}{\text{Largest possible } V_2 \quad \text{Smallest possible } V_1} = \frac{23.04}{13.35 - 10.35} = 7.20 \text{ g/mL}$$

Thus the calculated range is from 7.20 to 7.69 and the average of these values is 7.44. The error limit is the number that gives the high and low range values when added and subtracted from the average. Therefore, we can express the density as $7.44 \pm 0.25 \text{ g/mL}$, which is the average value plus or minus the quantity that gives the range calculated by assuming the largest uncertainties.

Analysis of the propagation of uncertainties is useful in drawing qualitative conclusions from the analysis of measurements. For example, suppose that we obtained the above results for the density of an unknown alloy and we want to know if it is one of the following alloys:

$$\text{Alloy A: } D = 7.58 \text{ g/mL}$$

$$\text{Alloy B: } D = 7.42 \text{ g/mL}$$

$$\text{Alloy C: } D = 8.56 \text{ g/mL}$$

We can safely conclude that the alloy is not C. But the values of the densities for alloys A and B are both within the inherent uncertainty of our method. To distinguish between A and B, we need to improve the precision of our determination: The obvious choice is to improve the precision of the volume measurement.

The worst-case method is very useful in estimating uncertainties when the results of several measurements are combined to calculate a result. We assume the maximum uncertainty in each measurement and calculate the minimum and maximum possible result. These extreme values describe the range and thus the error limit.

Appendix Two The Quantitative Kinetic Molecular Model

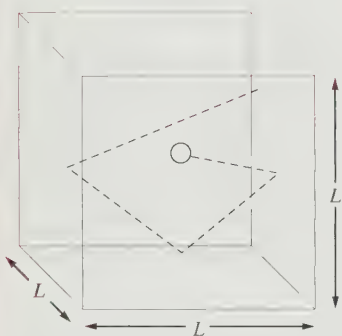


FIGURE A.3

An ideal gas particle in a cube whose sides are of length L . The particle collides elastically with the walls in a random, straightline motion.

We have seen that the kinetic molecular model successfully accounts for the properties of an ideal gas. This appendix will show in some detail how the postulates of the kinetic molecular model lead to an equation corresponding to the experimentally obtained ideal gas equation.

Recall that the particles of an ideal gas are assumed to be volumeless, to have no attraction for each other, and to produce pressure on their container by colliding with the container walls.

Suppose there are n moles of an ideal gas in a cubical container with sides each of length L . Assume each gas particle has a mass m and that it is in rapid, random, straight-line motion colliding with the walls, as shown in Fig. A.3. The collisions will be assumed to be *elastic*—no loss of kinetic energy occurs. We want to compute the force on the walls from the colliding gas particles and then, since pressure is force per unit area, to obtain an expression for the pressure of the gas.

Before we can derive the expression for the pressure of a gas, we must first discuss some characteristics of velocity. Each particle in the gas has a particular velocity u that can be divided into components u_x , u_y , and u_z , as shown in Fig. A.4. First, using u_x and u_y and the Pythagorean theorem, we can obtain u_{xy} as shown in Fig. A.4(c):

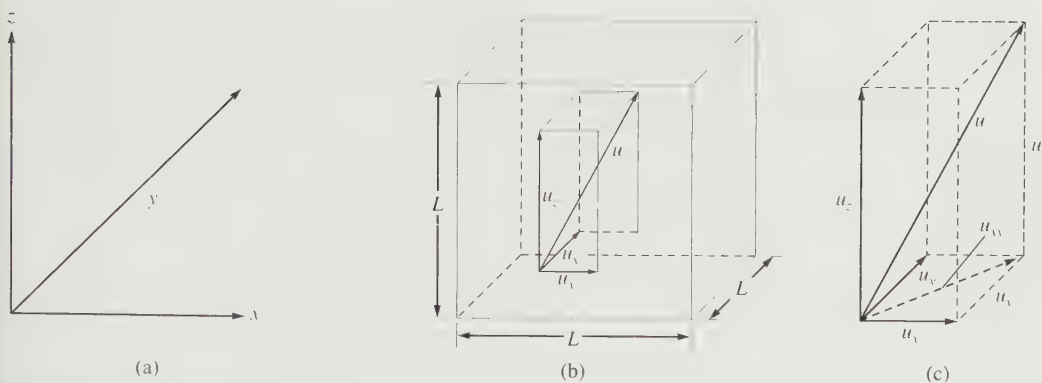
$$u_{xy}^2 = u_x^2 + u_y^2$$

↗ Hypotenuse of right triangle ↖ Sides of right triangle

Then, constructing another triangle as shown in Fig. A.4(c), we find

$$u^2 = u_{xy}^2 + u_z^2$$

$$\text{or } u^2 = \underbrace{u_x^2 + u_y^2}_{u_{xy}^2} + u_z^2$$

**FIGURE A.4**

(a) The Cartesian coordinate axes.

(b) The velocity u of any gas particle can be broken down into three mutually perpendicular components, u_x , u_y , and u_z . This can be represented as a rectangular solid with sides u_x , u_y , and u_z and body diagonal u .

(c) In the xy plane,

$$u_x^2 + u_y^2 = u_{xy}^2$$

by the Pythagorean theorem. Since u_{xy} and u_x are also perpendicular,

$$u^2 = u_{xy}^2 + u_z^2 = u_x^2 + u_y^2 + u_z^2$$

Now let's consider how an "average" gas particle moves. For example, how often does this particle strike the two walls of the box that are perpendicular to the x axis? It is important to realize that only the x component of the velocity affects the particle's impacts on these two walls, as shown in Fig. A.5(a). The larger the x component of the velocity, the faster the particle travels between these two walls, and the more impacts per unit of time it will make on these walls. Remember, the pressure of the gas is due to these collisions with the walls.

The collision frequency (collisions per unit of time) with the two walls that are perpendicular to the x axis is given by

$$\begin{aligned} (\text{Collision frequency})_x &= \frac{\text{velocity in the } x \text{ direction}}{\text{distance between the walls}} \\ &= \frac{u_x}{L} \end{aligned}$$

Next, what is the force of a collision? Force is defined as mass times acceleration (change in velocity per unit of time):

$$F = ma = m \left(\frac{\Delta u}{\Delta t} \right)$$

where F represents force, a represents acceleration, Δu represents a change in velocity, and Δt represents a given length of time.

Since we assume that the particle has constant mass, we can write

$$F = \frac{m\Delta u}{\Delta t} = \frac{\Delta(mu)}{\Delta t}$$

The quantity mu is the momentum of the particle (momentum is the product of mass and velocity), and the expression $F = \Delta(mu)/\Delta t$ implies that force is the change in momentum per unit of time. When a particle hits a wall perpendicular to the x axis, as shown in Fig. A.5(b), an elastic collision results in an *exact reversal* of the x component of velocity. That is, the *sign*, or direction, of u_x reverses when the particle

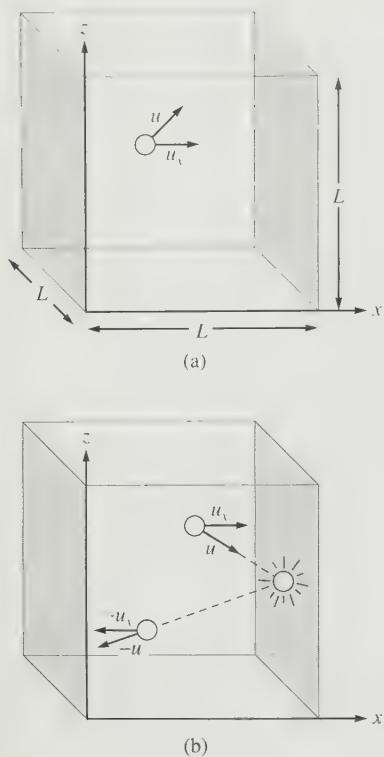


FIGURE A.5
(a) Only the x component of the gas particle's velocity affects the frequency of impacts on the shaded walls, the walls that are perpendicular to the x axis. (b) For an elastic collision, there is an exact reversal of the x component of the velocity and of the total velocity. The change in momentum (final – initial) is then

$$-mu_x - mu_x = -2mu_x$$

collides with one of the walls perpendicular to the x axis. Thus the final momentum is the *negative*, or opposite, of the initial momentum. Remember that an elastic collision means that there is no change in the *magnitude* of the velocity. The change in momentum in the x direction is then

$$\begin{aligned} \text{Change in momentum} &= \Delta(mu_x) = \text{final momentum} - \text{initial momentum} \\ &= -mu_x - mu_x \\ &\quad \begin{array}{cc} \nearrow & \nwarrow \\ \text{Final} & \text{Initial} \\ \text{momentum} & \text{momentum} \\ \text{in } x \text{ direction} & \text{in } x \text{ direction} \end{array} \\ &= -2mu_x \end{aligned}$$

But we are interested in the force the gas particle exerts on the walls of the box. Since we know that every action produces an equal but opposite reaction, the change in momentum with respect to the wall on impact is $-(-2mu_x)$, or $2mu_x$.

Recall that since force is the change in momentum per unit of time,

$$\text{Force}_x = \frac{\Delta(mu_x)}{\Delta t}$$

for the walls perpendicular to the x axis.

This expression can be obtained by multiplying the change in momentum per impact by the number of impacts per unit of time:

$$\begin{aligned} \text{Force}_x &= (2mu_x) \left(\frac{u_x}{L} \right) = \text{change in momentum per unit of time} \\ &\quad \begin{array}{cc} \nearrow & \nwarrow \\ \text{Change in momentum} & \text{Impacts per} \\ \text{per impact} & \text{unit of time} \end{array} \end{aligned}$$

That is,

$$\text{Force}_x = \frac{2mu_x^2}{L}$$

So far we have considered only the two walls of the box perpendicular to the x axis. We can assume that the force on the two walls perpendicular to the y axis is given by

$$\text{Force}_y = \frac{2mu_y^2}{L}$$

and that on the two walls perpendicular to the z axis by

$$\text{Force}_z = \frac{2mu_z^2}{L}$$

Since we have shown that

$$u^2 = u_x^2 + u_y^2 + u_z^2$$

the total force on the box is

$$\begin{aligned} \text{Force}_{\text{TOTAL}} &= \text{force}_x + \text{force}_y + \text{force}_z \\ &= \frac{2mu_x^2}{L} + \frac{2mu_y^2}{L} + \frac{2mu_z^2}{L} \\ &= \frac{2m}{L} (u_x^2 + u_y^2 + u_z^2) = \frac{2m}{L} (u^2) \end{aligned}$$

Now since we want the average force, we use the average of the square of the velocity ($\overline{u^2}$) to obtain

$$\overline{\text{Force}}_{\text{TOTAL}} = \frac{2m}{L}(\overline{u^2})$$

Next, we need to compute the pressure (force per unit of area)

$$\begin{aligned} \text{Pressure due to "average" particle} &= \frac{\overline{\text{force}}_{\text{TOTAL}}}{\text{area}_{\text{TOTAL}}} \\ &= \frac{2m\overline{u^2}}{6L^2} = \frac{m\overline{u^2}}{3L^3} \end{aligned}$$

↗
↖
 The 6 sides of the cube Area of each side

Since the volume V of the cube is equal to L^3 , we can write

$$\text{Pressure} = P = \frac{m\overline{u^2}}{3V}$$

So far we have considered the pressure on the walls due to a single, "average" particle. Of course, we want the pressure due to the entire gas sample. The number of particles in a given gas sample can be expressed as follows:

$$\text{Number of gas particles} = nN_A$$

where n is the number of moles and N_A is Avogadro's number.

The total pressure on the box due to n moles of a gas is therefore

$$P = nN_A \frac{m\overline{u^2}}{3V}$$

Next we want to express the pressure in terms of the kinetic energy of the gas molecules. Kinetic energy (the energy due to motion) is given by $\frac{1}{2}mu^2$, where m is the mass and u is the velocity. Since we are using the average of the velocity squared ($\overline{u^2}$), and since $m\overline{u^2} = 2(\frac{1}{2}m\overline{u^2})$, we have

$$P = \left(\frac{2}{3}\right) \frac{nN_A(\frac{1}{2}m\overline{u^2})}{V}$$

or

$$\frac{PV}{n} = \left(\frac{2}{3}\right) N_A(\frac{1}{2}m\overline{u^2})$$

Thus, based on the postulates of the kinetic molecular model, we have been able to derive an equation that has the same form as the ideal gas equation,

$$\frac{PV}{n} = RT$$

This agreement between experiment and theory supports the validity of the assumptions made in the kinetic molecular model about the behavior of gas particles, at least for the limiting case of an ideal gas.

Appendix Three Spectral Analysis

Although volumetric and gravimetric analyses are still very commonly used, spectroscopy is the technique most often used for modern chemical analysis. *Spectroscopy* is the study of electromagnetic radiation emitted or absorbed by a given chemical species. Since the quantity of radiation absorbed or emitted can be related to the quantity of the absorbing or emitting species present, this technique can be used for quantitative analysis. There are many spectroscopic techniques, as electromagnetic radiation spans a wide range of energies to include X rays, ultraviolet, infrared, and visible light, and microwaves, to name a few of its familiar forms. We will consider here only one procedure, which is based on the absorption of visible light.

If a liquid is colored, it is because some component of the liquid absorbs visible light. In a solution the greater the concentration of the light-absorbing substance, the more light absorbed, and the more intense the color of the solution.

The quantity of light absorbed by a substance can be measured by a *spectrophotometer*, shown schematically in Fig. A.6. This instrument consists of a source that emits all wavelengths of light in the visible region (wavelengths of ~ 400 to 700 nm); a monochromator, which selects a given wavelength of light; a sample holder for the solution being measured; and a detector, which compares the intensity of incident light I_0 to the intensity of light after it has passed through the sample I . The ratio I/I_0 , called the *transmittance*, is a measure of the fraction of light that passes through the sample. The amount of light absorbed is given by the *absorbance* A , where

$$A = -\log \frac{I}{I_0}$$

The absorbance can be expressed by the *Beer–Lambert law*:

$$A = \epsilon lc$$

where ϵ is the molar absorptivity or the molar extinction coefficient (in $\text{L/mol} \cdot \text{cm}$), l is the distance the light travels through the solution (in cm), and c is the concentration of the absorbing species (in mol/L). The Beer–Lambert law is the basis for using spectroscopy in quantitative analysis. If ϵ and l are known, measuring A for a solution allows us to calculate the concentration of the absorbing species in the solution.

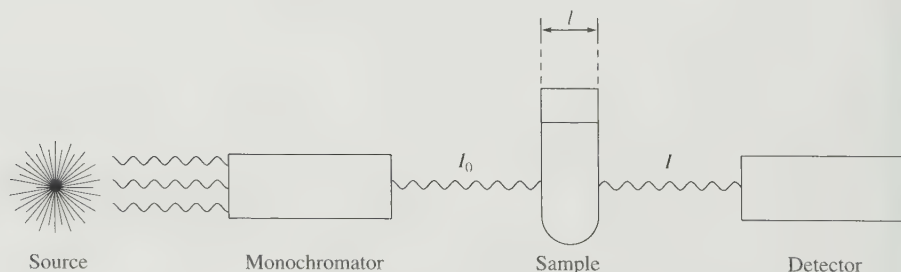


FIGURE A.6

A schematic diagram of a simple spectrophotometer. The source emits all wavelengths of visible light, which are dispersed using a prism or grating and then focused, one wavelength at a time, onto the sample. The detector compares the intensity of the incident light (I_0) to the intensity of the light after it has passed through the sample (I).

Suppose we have a pink solution containing an unknown concentration of $\text{Co}^{2+}(\text{aq})$ ions. A sample of this solution is placed in a spectrophotometer, and the absorbance is measured at a wavelength where ϵ for $\text{Co}^{2+}(\text{aq})$ is known to be $12 \text{ L/mol} \cdot \text{cm}$. The absorbance A is found to be 0.60. The width of the sample tube is 1.0 cm. We want to determine the concentration of $\text{Co}^{2+}(\text{aq})$ in the solution. This problem can be solved by a straightforward application of the Beer–Lambert law,

$$A = \epsilon lc$$

where

$$A = 0.60$$

$$\epsilon = \frac{12 \text{ L}}{\text{mol} \cdot \text{cm}}$$

$$l = \text{light path} = 1.0 \text{ cm}$$

Solving for the concentration gives

$$c = \frac{A}{\epsilon l} = \frac{0.60}{\left(12 \frac{\text{L}}{\text{mol} \cdot \text{cm}}\right)(1.0 \text{ cm})} = 5.0 \times 10^{-2} \text{ mol/L}$$

To obtain the unknown concentration of an absorbing species from the measured absorbance, we must know the product ϵl , since

$$c = \frac{A}{\epsilon l}$$

We can obtain the product ϵl by measuring the absorbance of a solution of *known* concentration, since

$$\epsilon l = \frac{A}{c}$$

Measured using a
spectrophotometer

Known from making up
the solution

However, a more accurate value of the product ϵl can be obtained by plotting A versus c for a series of solutions. Note that the equation $A = \epsilon lc$ gives a straight line with slope ϵl when A is plotted against c .

For example, consider the following typical spectroscopic analysis. A sample of steel from a bicycle frame is to be analyzed to determine its manganese content. The procedure involves weighing out a sample of the steel, dissolving it in strong acid, treating the resulting solution with a very strong oxidizing agent to convert all the manganese to permanganate ion (MnO_4^-), and then using spectroscopy to determine the concentration of the intensely purple MnO_4^- ions in the solution. To do this, however, the value of ϵl for MnO_4^- must be determined at an appropriate wavelength. The absorbance values for four solutions with known MnO_4^- concentrations were measured to give the following data:

Solution	Concentration of MnO_4^- (mol/L)	Absorbance
1	7.00×10^{-5}	0.175
2	1.00×10^{-4}	0.250
3	2.00×10^{-4}	0.500
4	3.50×10^{-4}	0.875

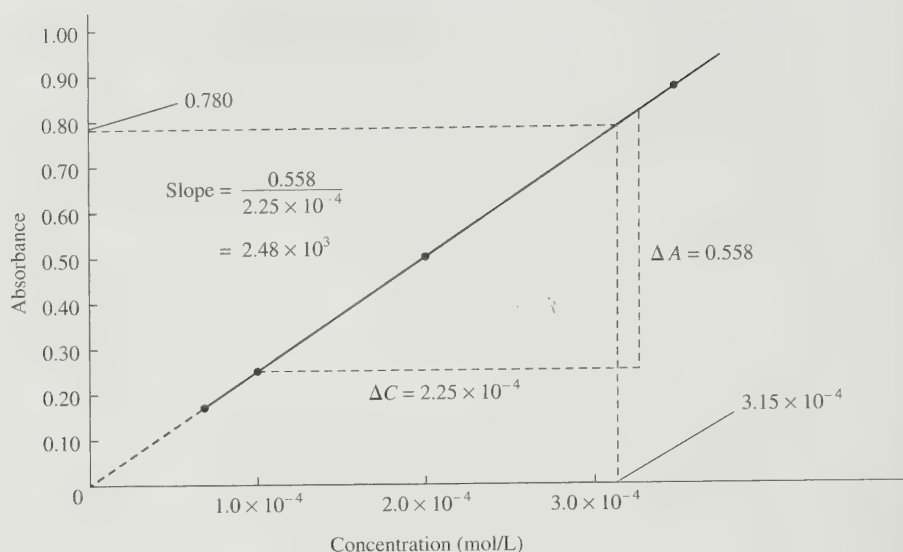


FIGURE A.7
A plot of absorbance versus concentration of MnO_4^- in a series of solutions of known concentration.

A plot of absorbance versus concentration for the solutions of known concentration is shown in Fig. A.7. The slope of this line (change in A /change in c) is $2.48 \times 10^3 \text{ L/mol}$. This quantity represents the product ϵl .

A sample of the steel weighing 0.1523 g was dissolved and the unknown amount of manganese was converted to MnO_4^- ions. Water was then added to give a solution with a final volume of 100.0 mL. A portion of this solution was placed in a spectrophotometer, and its absorbance was found to be 0.780. Using these data, we want to calculate the percent manganese in the steel. The MnO_4^- ions from the manganese in the dissolved steel sample show an absorbance of 0.780. Using the Beer-Lambert law, we calculate the concentration of MnO_4^- in this solution:

$$c = \frac{A}{\epsilon l} = \frac{0.780}{2.48 \times 10^3 \text{ L/mol}} \times 3.15 \times 10^{-4} \text{ mol/L}$$

There is a more direct way for finding c . Using a graph such as that in Fig. A.7 (often called a *Beer's law plot*), we can read the concentration that corresponds to $A = 0.780$. This interpolation is shown by dashed lines on the graph. By this method, $c = 3.15 \times 10^{-4} \text{ mol/L}$, which agrees with the value obtained above.

Recall that the original 0.1523-g steel sample was dissolved, the manganese was converted to permanganate, and the volume was adjusted to 100.0 mL. We now know that the $[\text{MnO}_4^-]$ in that solution is $3.15 \times 10^{-4} \text{ M}$. Using this concentration, we can calculate the total number of moles of MnO_4^- in that solution:

$$\begin{aligned} \text{mol of MnO}_4^- &= 100.0 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times 3.15 \times 10^{-4} \frac{\text{mol}}{\text{L}} \\ &= 3.15 \times 10^{-5} \text{ mol} \end{aligned}$$

Since each mole of manganese in the original steel sample yields a mole of MnO_4^- , that is,



the original steel sample must have contained $3.15 \times 10^{-5} \text{ mol}$ of manganese. The mass of manganese present in the sample is

$$3.15 \times 10^{-5} \text{ mol of Mn} \times \frac{54.938 \text{ g of Mn}}{1 \text{ mol of Mn}} = 1.73 \times 10^{-3} \text{ g of Mn}$$

Since the steel sample weighed 0.1523 g, the present manganese in the steel is

$$\frac{1.73 \times 10^{-3} \text{ g of Mn}}{1.523 \times 10^{-1} \text{ g of sample}} \times 100 = 1.14\%$$

This example illustrates a typical use of spectroscopy in quantitative analysis. The steps commonly involved are as follows:

1. Preparation of a calibration plot (a Beer's law plot) by measuring the absorbance values of a series of solutions with known concentrations.
2. Measurement of the absorbance of the solution of unknown concentration.
3. Use of the calibration plot to determine the unknown concentration.

Appendix Four Selected Thermodynamic Data

Note: All values are assumed precise to at least ± 1 .

Substance and State	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	S° (J/K · mol)
Aluminum			
Al(s)	0	0	28
Al ₂ O ₃ (s)	-1676	-1582	51
Al(OH) ₃ (s)	-1277		
AlCl ₃ (s)	-704	-629	111
Barium			
Ba(s)	0	0	67
BaCO ₃ (s)	-1219	-1139	112
BaO(s)	-582	-552	70
Ba(OH) ₂ (s)	-946		
BaSO ₄ (s)	-1465	-1353	132
Beryllium			
Be(s)	0	0	10
BeO(s)	-599	-569	14
Be(OH) ₂ (s)	-904	-815	47
Bromine			
Br ₂ (l)	0	0	152
Br ₂ (g)	31	3	245
Br ₂ (aq)	-3	4	130
Br ⁻ (aq)	-121	-104	82
HBr(g)	-36	-53	199
Cadmium			
Cd(s)	0	0	52
CdO(s)	-258	-228	55
Cd(OH) ₂ (s)	-561	-474	96
CdS(s)	-162	-156	65
CdSO ₄ (s)	-935	-823	123

Substance and State	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	S° (J/K · mol)
Calcium			
Ca(s)	0	0	41
CaC ₂ (s)	-63	-68	70
CaCO ₃ (s)	-1207	-1129	93
CaO(s)	-635	-604	40
Ca(OH) ₂ (s)	-987	-899	83
Ca ₃ (PO ₄) ₂ (s)	-4126	-3890	241
CaSO ₄ (s)	-1433	-1320	107
CaSiO ₃ (s)	-1630	-1550	84
Carbon			
C(s) (graphite)	0	0	6
C(s) (diamond)	2	3	2
CO(g)	-110.5	-137	198
CO ₂ (g)	-393.5	-394	214
CH ₄ (g)	-75	-51	186
CH ₃ OH(g)	-201	-163	240
CH ₃ OH(l)	-239	-166	127
H ₂ CO(g)	-116	-110	219
HCOOH(g)	-363	-351	249
HCN(g)	135.1	125	202
C ₂ H ₂ (g)	227	209	201
C ₂ H ₄ (g)	52	68	219
CH ₃ CHO(g)	-166	-129	250
C ₂ H ₅ OH(l)	-278	-175	161
C ₂ H ₆ (g)	-84.7	-32.9	229.5
C ₃ H ₆ (g)	20.9	62.7	266.9
C ₃ H ₈ (g)	-104	-24	270

(continued)

Appendix Four (continued)

Substance and State	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	S° (J/K · mol)
Carbon, <i>continued</i>			
C ₂ H ₄ O(g) (ethylene oxide)	-53	-13	242
CH ₂ =CHCN(g)	185.0	195.4	274
CH ₃ COOH(l)	-484	-389	160
C ₆ H ₁₂ O ₆ (s)	-1275	-911	212
CCl ₄	-135	-65	216
Chlorine			
Cl ₂ (g)	0	0	223
Cl ₂ (aq)	-23	7	121
Cl ⁻ (aq)	-167	-131	57
HCl(g)	-92	-95	187
Chromium			
Cr(s)	0	0	24
Cr ₂ O ₃ (s)	-1128	-1047	81
CrO ₃ (s)	-579	-502	72
Copper			
Cu(s)	0	0	33
CuCO ₃ (s)	-595	-518	88
Cu ₂ O(s)	-170	-148	93
CuO(s)	-156	-128	43
Cu(OH) ₂ (s)	-450	-372	108
CuS(s)	-49	-49	67
Fluorine			
F ₂ (g)	0	0	203
F ⁻ (aq)	-333	-279	-14
HF(g)	-271	-273	174
Hydrogen			
H ₂ (g)	0	0	131
H(g)	217	203	115
H ⁺ (aq)	0	0	0
OH ⁻ (aq)	-230	-157	-11
H ₂ O(l)	-286	-237	70
H ₂ O(g)	-242	-229	189
Iodine			
I ₂ (s)	0	0	116
I ₂ (g)	62	19	261
I ₂ (aq)	23	16	137
I ⁻ (aq)	-55	-52	106
Iron			
Fe(s)	0	0	27
Fe ₃ C(s)	21	15	108
Fe _{0.95} O(s) (wustite)	-264	-240	59
FeO	-272	-255	61
Fe ₃ O ₄ (s) (magnetite)	-1117	-1013	146
Fe ₂ O ₃ (s) (hematite)	-826	-740	90
FeS(s)	-95	-97	67
FeS ₂ (s)	-178	-166	53
FeSO ₄ (s)	-929	-825	121

Substance and State	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	S° (J/K · mol)
Lead			
Pb(s)	0	0	65
PbO ₂ (s)	-277	-217	69
PbS(s)	-100	-99	91
PbSO ₄ (s)	-920	-813	149
Magnesium			
Mg(s)	0	0	33
MgCO ₃ (s)	-1113	-1029	66
MgO(s)	-602	-569	27
Mg(OH) ₂ (s)	-925	-834	64
Manganese			
Mn(s)	0	0	32
MnO(s)	-385	-363	60
Mn ₃ O ₄ (s)	-1387	-1280	149
Mn ₂ O ₃ (s)	-971	-893	110
MnO ₂ (s)	-521	-466	53
MnO ₄ ⁻ (aq)	-543	-449	190
Mercury			
Hg(l)	0	0	76
Hg ₂ Cl ₂ (s)	-265	-211	196
HgCl ₂ (s)	-230	-184	144
HgO(s)	-90	-59	70
HgS(s)	-58	-49	78
Nickel			
Ni(s)	0	0	30
NiCl ₂ (s)	-316	-272	107
NiO(s)	-241	-213	38
Ni(OH) ₂ (s)	-538	-453	79
NiS(s)	-93	-90	53
Nitrogen			
N ₂ (g)	0	0	192
NH ₃ (g)	-46	-17	193
NH ₃ (aq)	-80	-27	111
NH ₄ ⁺ (aq)	-132	-79	113
NO(g)	90	87	211
NO ₂ (g)	34	52	240
N ₂ O(g)	82	104	220
N ₂ O ₄ (g)	10	98	304
N ₂ O ₄ (l)	-20	97	209
N ₂ O ₅ (s)	-42	134	178
N ₂ H ₄ (l)	51	149	121
N ₂ H ₃ CH ₃ (l)	54	180	166
HNO ₃ (aq)	-207	-111	146
HNO ₃ (l)	-174	-81	156
NH ₄ ClO ₄ (s)	-295	-89	186
NH ₄ Cl(s)	-314	-203	96
Oxygen			
O ₂ (g)	0	0	205
O(g)	249	232	161
O ₃ (g)	143	163	239

Appendix Four (continued)

Substance and State	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	S° (J/K · mol)
Phosphorus			
P(s) (white)	0	0	41
P(s) (red)	-18	-12	23
P(s) (black)	-39	-33	23
P ₄ (g)	59	24	280
PF ₃ (g)	-1578	-1509	296
PH ₃ (g)	5	13	210
H ₃ PO ₄ (s)	-1279	-1119	110
H ₃ PO ₄ (l)	-1267	—	—
H ₃ PO ₄ (aq)	-1288	-1143	158
P ₄ O ₁₀ (s)	-2984	-2698	229
Potassium			
K(s)	0	0	64
KCl(s)	-436	-408	83
KClO ₃ (s)	-391	-290	143
KClO ₄ (s)	-433	-304	151
K ₂ O(s)	-361	-322	98
K ₂ O ₂ (s)	-496	-430	113
KO ₂ (s)	-283	-238	117
KOH(s)	-425	-379	79
KOH(aq)	-481	-440	9.20
Silicon			
SiO ₂ (s) (quartz)	-911	-856	42
SiCl ₄ (l)	-687	-620	240
Silver			
Ag(s)	0	0	43
Ag ⁺ (aq)	105	77	73
AgBr(s)	-100	-97	107
AgCN(s)	146	164	84
AgCl(s)	-127	-110	96
Ag ₂ CrO ₄ (s)	-712	-622	217
AgI(s)	-62	-66	115
Ag ₂ O(s)	-31	-11	122
Ag ₂ S(s)	-32	-40	146
Sodium			
Na(s)	0	0	51
Na ⁺ (aq)	-240	-262	59
NaBr(s)	-360	-347	84
Na ₂ CO ₃ (s)	-1131	-1048	136
NaHCO ₃ (s)	-948	-852	102
NaCl(s)	-411	-384	72
NaH(s)	-56	-33	40
NaI(s)	-288	-282	91
NaNO ₂ (s)	-359	—	—
NaNO ₃ (s)	-467	-366	116

Substance and State	ΔH_f° (kJ/mol)	ΔG_f° (kJ/mol)	S° (J/K · mol)
Sodium, <i>continued</i>			
Na ₂ O(s)	-416	-377	73
Na ₂ O ₂ (s)	-515	-451	95
NaOH(s)	-427	-381	64
NaOH(aq)	-470	-419	50
Sulfur			
S(s) (rhombic)	0	0	32
S(s) (monoclinic)	0.3	0.1	33
S ²⁻ (aq)	33	86	-15
S ₈ (g)	102	50	431
SF ₆ (g)	-1209	-1105	292
H ₂ S(g)	-21	-34	206
SO ₂ (g)	-297	-300	248
SO ₃ (g)	-396	-371	257
SO ₄ ²⁻ (aq)	-909	-745	20
H ₂ SO ₄ (l)	-814	-690	157
H ₂ SO ₄ (aq)	-909	-745	20
Tin			
Sn(s) (white)	0	0	52
Sn(s) (gray)	-2	0.1	44
SnO(s)	-285	-257	56
SnO ₂ (s)	-581	-520	52
Sn(OH) ₂ (s)	-561	-492	155
Titanium			
TiCl ₄ (g)	-763	-727	355
TiO ₂ (s)	-945	-890	50
Uranium			
U(s)	0	0	50
UF ₆ (s)	-2137	-2008	228
UF ₆ (g)	-2113	-2029	380
UO ₂ (s)	-1084	-1029	78
U ₃ O ₈ (s)	-3575	-3393	282
UO ₃ (s)	-1230	-1150	99
Xenon			
Xe(g)	0	0	170
XeF ₂ (g)	-108	-48	254
XeF ₄ (s)	-251	-121	146
XeF ₆ (g)	-294	—	—
XeO ₃ (s)	402	—	—
Zinc			
Zn(s)	0	0	42
ZnO(s)	-348	-318	44
Zn(OH) ₂ (s)	-642	—	—
ZnS(s) (wurtzite)	-193	—	—
ZnS(s) (zinc blende)	-206	-201	58
ZnSO ₄ (s)	-983	-874	120

Appendix Five Equilibrium Constants and Reduction Potentials

A5.1 Values of K_a for Some Common Monoprotic Acids

Name	Formula	Value of K_a
Hydrogen sulfate ion	HSO_4^-	1.2×10^{-2}
Chlorous acid	HClO_2	1.2×10^{-2}
Monochloroacetic acid	$\text{HC}_2\text{H}_2\text{ClO}_2$	1.35×10^{-3}
Hydrofluoric acid	HF	7.2×10^{-4}
Nitrous acid	HNO_2	4.0×10^{-4}
Formic acid	HCO_2H	1.8×10^{-4}
Lactic acid	$\text{HC}_3\text{H}_5\text{O}_3$	1.38×10^{-4}
Benzoic acid	$\text{HC}_7\text{H}_5\text{O}_2$	6.4×10^{-5}
Acetic acid	$\text{HC}_2\text{H}_3\text{O}_2$	1.8×10^{-5}
Hydrated aluminum(III) ion	$[\text{Al}(\text{H}_2\text{O})_6]^{3+}$	1.4×10^{-5}
Propanoic acid	$\text{HC}_3\text{H}_5\text{O}_2$	1.3×10^{-5}
Hypochlorous acid	HOCl	3.5×10^{-8}
Hypobromous acid	HOBr	2×10^{-9}
Hydrocyanic acid	HCN	6.2×10^{-10}
Boric acid	H_3BO_3	5.8×10^{-10}
Ammonium ion	NH_4^+	5.6×10^{-10}
Phenol	HOC_6H_5	1.6×10^{-10}
Hypoiodous acid	HOI	2×10^{-11}

A5.2 Stepwise Dissociation Constants for Several Common Polyprotic Acids

Name	Formula	K_{a1}	K_{a2}	K_{a3}
Phosphoric acid	H_3PO_4	7.5×10^{-3}	6.2×10^{-8}	4.8×10^{-13}
Arsenic acid	H_3AsO_4	5×10^{-3}	8×10^{-8}	6×10^{-10}
Carbonic acid	H_2CO_3	4.3×10^{-7}	5.6×10^{-11}	
Sulfuric acid	H_2SO_4	Large	1.2×10^{-2}	
Sulfurous acid	H_2SO_3	1.5×10^{-2}	1.0×10^{-7}	
Hydrosulfuric acid	H_2S	1.0×10^{-7}	$\sim 10^{-19}$	
Oxalic acid	$\text{H}_2\text{C}_2\text{O}_4$	6.5×10^{-2}	6.1×10^{-5}	
Ascorbic acid (vitamin C)	$\text{H}_2\text{C}_6\text{H}_6\text{O}_6$	7.9×10^{-5}	1.6×10^{-12}	
Citric acid	$\text{H}_3\text{C}_6\text{H}_5\text{O}_7$	8.4×10^{-4}	1.8×10^{-5}	4.0×10^{-6}

A5.3 Values of K_b for Some Common Weak Bases

Name	Formula	Conjugate Acid	K_b
Ammonia	NH_3	NH_4^+	1.8×10^{-5}
Methylamine	CH_3NH_2	CH_3NH_3^+	4.38×10^{-4}
Ethylamine	$\text{C}_2\text{H}_5\text{NH}_2$	$\text{C}_2\text{H}_5\text{NH}_3^+$	5.6×10^{-4}
Diethylamine	$(\text{C}_2\text{H}_5)_2\text{NH}$	$(\text{C}_2\text{H}_5)_2\text{NH}_2^+$	1.3×10^{-3}
Triethylamine	$(\text{C}_2\text{H}_5)_3\text{N}$	$(\text{C}_2\text{H}_5)_3\text{NH}^+$	4.0×10^{-4}
Hydroxylamine	HONH_2	HONH_3^+	1.1×10^{-8}
Hydrazine	H_2NNH_2	H_2NNH_3^+	3.0×10^{-6}
Aniline	$\text{C}_6\text{H}_5\text{NH}_2$	$\text{C}_6\text{H}_5\text{NH}_3^+$	3.8×10^{-10}
Pyridine	$\text{C}_5\text{H}_5\text{N}$	$\text{C}_5\text{H}_5\text{NH}^+$	1.7×10^{-9}

A5.4 K_{sp} Values at 25°C for Common Ionic Solids

Ionic Solid	K_{sp} (at 25°C)	Ionic Solid	K_{sp} (at 25°C)	Ionic Solid	K_{sp} (at 25°C)
Fluorides		$\text{Hg}_2\text{CrO}_4^*$	2×10^{-9}	$\text{Co}(\text{OH})_2$	2.5×10^{-16}
BaF_2	2.4×10^{-5}	BaCrO_4	8.5×10^{-11}	$\text{Ni}(\text{OH})_2$	1.6×10^{-16}
MgF_2	6.4×10^{-9}	Ag_2CrO_4	9.0×10^{-12}	$\text{Zn}(\text{OH})_2$	4.5×10^{-17}
PbF_2	4×10^{-8}	PbCrO_4	2×10^{-16}	$\text{Cu}(\text{OH})_2$	1.6×10^{-19}
SrF_2	7.9×10^{-10}			$\text{Hg}(\text{OH})_2$	3×10^{-26}
CaF_2	4.0×10^{-11}	Carbonates		$\text{Sn}(\text{OH})_2$	3×10^{-27}
Chlorides		NiCO_3	1.4×10^{-7}	$\text{Cr}(\text{OH})_3$	6.7×10^{-31}
PbCl_2	1.6×10^{-5}	CaCO_3	8.7×10^{-9}	$\text{Al}(\text{OH})_3$	2×10^{-32}
AgCl	1.6×10^{-10}	BaCO_3	1.6×10^{-9}	$\text{Fe}(\text{OH})_3$	4×10^{-38}
Hg_2Cl_2^*	1.1×10^{-18}	SrCO_3	7×10^{-10}	$\text{Co}(\text{OH})_3$	2.5×10^{-43}
Bromides		CuCO_3	2.5×10^{-10}	Sulfides	
PbBr_2	4.6×10^{-6}	ZnCO_3	2×10^{-10}	MnS	2.3×10^{-13}
AgBr	5.0×10^{-13}	MnCO_3	8.8×10^{-11}	FeS	3.7×10^{-19}
Hg_2Br_2^*	1.3×10^{-22}	FeCO_3	2.1×10^{-11}	NiS	3×10^{-21}
Iodides		Ag_2CO_3	8.1×10^{-12}	CoS	5×10^{-22}
PbI_2	1.4×10^{-8}	CdCO_3	5.2×10^{-12}	ZnS	2.5×10^{-22}
AgI	1.5×10^{-16}	PbCO_3	1.5×10^{-15}	SnS	1×10^{-26}
Hg_2I_2^*	4.5×10^{-29}	MgCO_3	1×10^{-5}	CdS	1.0×10^{-28}
Sulfates		Hg_2CO_3^*	9.0×10^{-15}	PbS	7×10^{-29}
CaSO_4	6.1×10^{-5}	Hydroxides		CuS	8.5×10^{-45}
Ag_2SO_4	1.2×10^{-5}	$\text{Ba}(\text{OH})_2$	5.0×10^{-3}	Ag_2S	1.6×10^{-49}
SrSO_4	3.2×10^{-7}	$\text{Sr}(\text{OH})_2$	3.2×10^{-4}	HgS	1.6×10^{-54}
PbSO_4	1.3×10^{-8}	$\text{Ca}(\text{OH})_2$	1.3×10^{-6}	Phosphates	
BaSO_4	1.5×10^{-9}	AgOH	2.0×10^{-8}	Ag_3PO_4	1.8×10^{-18}
Chromates		$\text{Mg}(\text{OH})_2$	8.9×10^{-12}	$\text{Sr}_3(\text{PO}_4)_2$	1×10^{-31}
SrCrO_4	3.6×10^{-5}	$\text{Mn}(\text{OH})_2$	2×10^{-13}	$\text{Ca}_3(\text{PO}_4)_2$	1.3×10^{-32}
		$\text{Cd}(\text{OH})_2$	5.9×10^{-15}	$\text{Ba}_3(\text{PO}_4)_2$	6×10^{-39}
		$\text{Pb}(\text{OH})_2$	1.2×10^{-15}	$\text{Pb}_3(\text{PO}_4)_2$	1×10^{-54}
		$\text{Fe}(\text{OH})_2$	1.8×10^{-15}		

*Contains Hg_2^{2+} ions. $K_{sp} = [\text{Hg}_2^{2+}][\text{X}^-]^2$ for Hg_2X_2 salts.

A5.5 Standard Reduction Potentials at 25°C (298 K) for Many Common Half-Reactions

Half-Reaction	E° (V)	Half-Reaction	E° (V)
$F_2 + 2e^- \rightarrow 2F^-$	2.87	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	0.40
$Ag^+ + e^- \rightarrow Ag$	1.99	$Cu^{2+} + 2e^- \rightarrow Cu$	0.34
$Co^{3+} + e^- \rightarrow Co^{2+}$	1.82	$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$	0.34
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.78	$AgCl + e^- \rightarrow Ag + Cl^-$	0.22
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	1.70	$SO_4^{2-} + 4H^+ + 2e^- \rightarrow H_2SO_3 + H_2O$	0.20
$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$	1.69	$Cu^{2+} + e^- \rightarrow Cu^+$	0.16
$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$	1.68	$2H^+ + 2e^- \rightarrow H_2$	0.00
$2e^- + 2H^+ + IO_4^- \rightarrow IO_3^- + H_2O$	1.60	$Fe^{3+} + 3e^- \rightarrow Fe$	-0.036
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	1.51	$Pb^{2+} + 2e^- \rightarrow Pb$	-0.13
$Au^{3+} + 3e^- \rightarrow Au$	1.50	$Sn^{2+} + 2e^- \rightarrow Sn$	-0.14
$PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$	1.46	$Ni^{2+} + 2e^- \rightarrow Ni$	-0.23
$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36	$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	-0.35
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	1.33	$Cd^{2+} + 2e^- \rightarrow Cd$	-0.40
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.23	$Fe^{2+} + 2e^- \rightarrow Fe$	-0.44
$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	1.21	$Cr^{3+} + e^- \rightarrow Cr^{2+}$	-0.50
$IO_3^- + 6H^+ + 5e^- \rightarrow \frac{1}{2}I_2 + 3H_2O$	1.20	$Cr^{3+} + 3e^- \rightarrow Cr$	-0.73
$Br_2 + 2e^- \rightarrow 2Br^-$	1.09	$Zn^{2+} + 2e^- \rightarrow Zn$	-0.76
$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$	1.00	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	-0.83
$AuCl_4^- + 3e^- \rightarrow Au + 4Cl^-$	0.99	$Mn^{2+} + 2e^- \rightarrow Mn$	-1.18
$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	0.96	$Al^{3+} + 3e^- \rightarrow Al$	-1.66
$ClO_2 + e^- \rightarrow ClO_2^-$	0.954	$H_2 + 2e^- \rightarrow 2H^-$	-2.23
$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$	0.91	$Mg^{2+} + 2e^- \rightarrow Mg$	-2.37
$Ag^+ + e^- \rightarrow Ag$	0.80	$La^{3+} + 3e^- \rightarrow La$	-2.37
$Hg_2^{2+} + 2e^- \rightarrow 2Hg$	0.80	$Na^+ + e^- \rightarrow Na$	-2.71
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.77	$Ca^{2+} + 2e^- \rightarrow Ca$	-2.76
$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	0.68	$Ba^{2+} + 2e^- \rightarrow Ba$	-2.90
$MnO_4^- + e^- \rightarrow MnO_4^{2-}$	0.56	$K^+ + e^- \rightarrow K$	-2.92
$I_2 + 2e^- \rightarrow 2I^-$	0.54	$Li^+ + e^- \rightarrow Li$	-3.05
$Cu^+ + e^- \rightarrow Cu$	0.52		

Appendix Six SI Units and Conversion Factors

Length

SI unit: meter (m)

1 meter	= 1.0936 yards
1 centimeter	= 0.39370 inch
1 inch	= 2.54 centimeters (exactly)
1 kilometer	= 0.62137 mile
1 mile	= 5280 feet = 1.6093 kilometers
1 angstrom	= 10^{-10} meter = 100 picometers

Mass

SI unit: kilogram (kg)

1 kilogram	= 1000 grams = 2.2046 pounds
1 pound	= 453.59 grams = 0.45359 kilogram = 16 ounces
1 ton	= 2000 pounds = 907.185 kilograms
1 metric ton	= 1000 kilograms = 2204.6 pounds
1 atomic mass unit	= 1.66056×10^{-27} kilograms

Volume

SI unit: cubic meter (m^3)

1 liter	= $10^{-3} m^3$ = 1 dm^3 = 1.0567 quarts
1 gallon	= 4 quarts = 8 pints = 3.7854 liters
1 quart	= 32 fluid ounces = 0.94633 liter

Temperature

SI unit: kelvin (K)

0 K	= $-273.15^\circ C$ = $-459.67^\circ F$
K	= $^\circ C + 273.15$
$^\circ C$	= $\frac{5}{9}(^\circ F - 32)$
$^\circ F$	= $\frac{9}{5}(^\circ C) + 32$

Energy

SI unit: joule (J)

1 joule	= $1 kg \cdot m^2/s^2$ = 0.23901 calorie = 9.4781×10^{-4} btu (British thermal unit)
1 calorie	= 4.184 joules = 3.965×10^{-3} btu
1 btu	= 1055.06 joules = 252.2 calories

Pressure

SI unit: pascal (Pa)

1 pascal	= $1 N/m^2$ = $1 kg/m \cdot s^2$
1 atmosphere	= 101.325 kilopascals = 760 torr (mmHg) = 14.70 pounds per square inch
1 bar	= 10^5 pascals

Glossary

- Accuracy** the agreement of a particular value with the true value. (1.4)
- Acid** a substance that produces hydrogen ions in solution; a proton donor. (2.8; 4.2; 4.8)
- Acid–base indicator** a substance that marks the end point of an acid–base titration by changing color. (15.5)
- Acid dissociation constant (K_a)** the equilibrium constant for a reaction in which a proton is removed from an acid by H_2O to form the conjugate base and H_3O^+ . (14.1)
- Acid rain** a result of air pollution by sulfur dioxide. (5.9)
- Acidic oxide** a covalent oxide that dissolves in water to give an acidic solution. (14.10)
- Actinide series** a group of 14 elements following actinium in the periodic table, in which the $5f$ orbitals are being filled. (7.11; 19.1)
- Activated complex (transition state)** the arrangement of atoms found at the top of the potential energy barrier as a reaction proceeds from reactants to products. (12.7)
- Activation energy** the threshold energy that must be overcome to produce a chemical reaction. (12.7)
- Addition polymerization** a type of polymerization in which the monomers simply add together to form the polymer, with no other products. (22.5)
- Addition reaction** a reaction in which atoms add to a carbon–carbon multiple bond. (22.2)
- Adsorption** the collection of one substance on the surface of another. (12.8)
- Air pollution** contamination of the atmosphere, mainly by the gaseous products of transportation and production of electricity. (5.9)
- Alcohol** an organic compound in which the hydroxyl group is a substituent on a hydrocarbon. (22.4)
- Aldehyde** an organic compound containing the carbonyl group bonded to at least one hydrogen atom. (22.4)
- Alkali metal** a Group 1A metal. (2.7; 19.2)
- Alkaline earth metal** a Group 2A metal. (2.7; 19.4)
- Alkane** a saturated hydrocarbon with the general formula C_nH_{2n+2} . (22.1)
- Alkene** an unsaturated hydrocarbon containing a carbon–carbon double bond. The general formula is C_nH_{2n} . (22.2)
- Alkyne** an unsaturated hydrocarbon containing a triple carbon–carbon bond. The general formula is C_nH_{2n-2} . (22.2)
- Alloy** a substance that contains a mixture of elements and has metallic properties. (10.4)
- Alloy steel** a form of steel containing carbon plus other metals such as chromium, cobalt, manganese, and molybdenum. (21.8)
- Alpha (α) particle** a helium nucleus. (18.1)
- Alpha-particle production** a common mode of decay for radioactive nuclides in which the mass number changes. (18.1)
- Amine** an organic base derived from ammonia in which one or more of the hydrogen atoms are replaced by organic groups. (14.6; 22.4)
- α -Amino acid** an organic acid in which an amino group and an R group are attached to the carbon atom next to the carboxyl group. (22.6)
- Amorphous solid** a solid with considerable disorder in its structure. (10.3)
- Ampere** the unit of electric current equal to one coulomb of charge per second. (17.7)
- Amphoteric substance** a substance that can behave either as an acid or as a base. (14.2)
- Angular momentum quantum number (ℓ)** the quantum number relating to the shape of an atomic orbital, which can assume any integral value from 0 to $n - 1$ for each value of n . (7.6)
- Anion** a negative ion. (2.6)
- Anode** the electrode in a galvanic cell at which oxidation occurs. (17.1)
- Antibonding molecular orbital** an orbital higher in energy than the atomic orbitals of which it is composed. (9.2)
- Aqueous solution** a solution in which water is the dissolving medium or solvent. (4)
- Aromatic hydrocarbon** one of a special class of cyclic unsaturated hydrocarbons, the simplest of which is benzene. (22.3)
- Arrhenius concept** a concept postulating that acids produce hydrogen ions in aqueous solution, while bases produce hydroxide ions. (14.1)
- Arrhenius equation** the equation representing the rate constant as $k = Ae^{-E_a/RT}$, where A represents the product of the collision frequency and the steric factor, and $e^{-E_a/RT}$ is the fraction of collisions with sufficient energy to produce a reaction. (12.7)
- Atactic chain** a polymer chain in which the substituent groups such as CH_3 are randomly distributed along the chain. (22.5)
- Atmosphere** the mixture of gases that surrounds the earth's surface. (5.9)
- Atomic number** the number of protons in the nucleus of an atom. (2.5; 18)
- Atomic radius** half the distance between the nuclei in a molecule consisting of identical atoms. (7.12)
- Atomic solid** a solid that contains atoms at the lattice points. (10.3)
- Atomic weight** the weighted average mass of the atoms in a naturally occurring element. (2.3)
- Aufbau principle** the principle stating that as protons are added one by one to the nucleus to build up the elements, electrons are similarly added to hydrogen-like orbitals. (7.11)
- Autoionization** the transfer of a proton from one molecule to another of the same substance. (14.2)
- Avogadro's law** equal volumes of gases at the same temperature and pressure contain the same number of particles. (5.2)

Avogadro's number the number of atoms in exactly 12 grams of pure ^{12}C , equal to 6.022×10^{23} . (3.2)

Ball-and-stick model a molecular model that distorts the sizes of atoms but shows bond relationships clearly. (2.6)

Band model a molecular model for metals in which the electrons are assumed to travel around the metal crystal in molecular orbitals formed from the valence atomic orbitals of the metal atoms. (10.4)

Barometer a device for measuring atmospheric pressure. (5.1)

Base a substance that produces hydroxide ions in aqueous solution, a proton acceptor. (4.8)

Basic oxide an ionic oxide that dissolves in water to produce a basic solution. (14.10)

Basic oxygen process a process for producing steel by oxidizing and removing the impurities in iron using a high-pressure blast of oxygen. (21.8)

Battery a group of galvanic cells connected in series. (17.5)

Beta (β) particle an electron produced in radioactive decay. (18.1)

Beta-particle production a decay process for radioactive nuclides in which the mass number remains constant and the atomic number changes. The net effect is to change a neutron to a proton. (18.1)

Bidentate ligand a ligand that can form two bonds to a metal ion. (21.3)

Bimolecular step a reaction involving the collision of two molecules. (12.6)

Binary compound a two-element compound. (2.8)

Binding energy (nuclear) the energy required to decompose a nucleus into its component nucleons. (18.5)

Biomolecule a molecule responsible for maintaining and/or reproducing life. (22)

Blast furnace a furnace in which iron oxide is reduced to iron metal by using a very strong blast of hot air to produce carbon monoxide from coke, and then using this gas as a reducing agent for the iron. (21.8)

Bond energy the energy required to break a given chemical bond. (8.1)

Bond length the distance between the nuclei of the two atoms connected by a bond; the distance where the total energy of a diatomic molecule is minimal. (8.1)

Bond order the difference between the number of bonding electrons and the number of antibonding electrons, divided by two. It is an index of bond strength. (9.2)

Bonding molecular orbital an orbital lower in energy than the atomic orbitals of which it is composed. (9.2)

Bonding pair an electron pair found in the space between two atoms. (8.9)

Borane a covalent hydride of boron. (19.5)

Boyle's law the volume of a given sample of gas at constant temperature varies inversely with the pressure. (5.2)

Breeder reactor a nuclear reactor in which fissionable fuel is produced while the reactor runs. (18.6)

Brønsted-Lowry model a model proposing that an acid is a proton donor, and a base is a proton acceptor. (14.1)

Buffered solution a solution that resists a change in its pH when either hydroxide ions or protons are added. (15.2)

Buffering capacity the ability of a buffered solution to absorb protons or hydroxide ions without a significant change in pH; determined by the magnitudes of $[\text{HA}]$ and $[\text{A}^-]$ in the solution. (15.3)

Calorimetry the science of measuring heat flow. (6.2)

Capillary action the spontaneous rising of a liquid in a narrow tube. (10.2)

Carbohydrate a polyhydroxyl ketone or polyhydroxyl aldehyde or a polymer composed of these. (22.6)

Carbon steel an alloy of iron containing up to about 1.5% carbon. (21.8)

Carboxyhemoglobin a stable complex of hemoglobin and carbon monoxide that prevents normal oxygen uptake in the blood. (21.7)

Carboxyl group the $-\text{COOH}$ group in an organic acid. (14.2; 22.4)

Carboxylic acid an organic compound containing the carboxyl group; an acid with the general formula RCOOH . (22.4)

Catalyst a substance that speeds up a reaction without being consumed. (12.8)

Cathode the electrode in a galvanic cell at which reduction occurs. (17.1)

Cathode rays the "rays" emanating from the negative electrode (cathode) in a partially evacuated tube; a stream of electrons. (2.4)

Cathodic protection a method in which an active metal, such as magnesium, is connected to steel to protect it from corrosion. (17.6)

Cation a positive ion. (2.6)

Cell potential (electromotive force) the driving force in a galvanic cell that pulls electrons from the reducing agent in one compartment to the oxidizing agent in the other. (17.1)

Ceramic a nonmetallic material made from clay and hardened by firing at high temperature; it contains minute silicate crystals suspended in a glassy cement. (10.5)

Chain reaction (nuclear) a self-sustaining fission process caused by the production of neutrons that proceed to split other nuclei. (18.6)

Charles's law the volume of a given sample of gas at constant pressure is directly proportional to the temperature in kelvins. (5.2)

Chelating ligand (chelate) a ligand having more than one atom with a lone pair that can be used to bond to a metal ion. (21.3)

Chemical bond the force or, more accurately, the energy, that holds two atoms together in a compound. (2.6)

Chemical change the change of substances into other substances through a reorganization of the atoms; a chemical reaction. (1.9)

Chemical equation a representation of a chemical reaction showing the relative numbers of reactant and product molecules. (3.6)

Chemical equilibrium a dynamic reaction system in which the concentrations of all reactants and products remain constant as a function of time. (13)

- Chemical formula** the representation of a molecule in which the symbols for the elements are used to indicate the types of atoms present and subscripts are used to show the relative numbers of atoms. (2.6)
- Chemical kinetics** the area of chemistry that concerns reaction rates. (12)
- Chemical stoichiometry** the calculation of the quantities of material consumed and produced in chemical reactions. (3)
- Chirality** the quality of having nonsuperimposable mirror images. (21.4)
- Chlor-alkali process** the process for producing chlorine and sodium hydroxide by electrolyzing brine in a mercury cell. (17.8)
- Chromatography** the general name for a series of methods for separating mixtures by employing a system with a mobile phase and a stationary phase. (1.9)
- Coagulation** the destruction of a colloid by causing particles to aggregate and settle out. (11.8)
- Codons** organic bases in sets of three that form the genetic code. (22.6)
- Colligative properties** properties of a solution that depend only on the number, and not on the identity, of the solute particles. (11.5)
- Collision model** a model based on the idea that molecules must collide to react; used to account for the observed characteristics of reaction rates. (12.7)
- Colloid (colloidal dispersion)** a suspension of particles in a dispersing medium. (11.8)
- Combustion reaction** the vigorous and exothermic reaction that takes place between certain substances, particularly organic compounds, and oxygen. (22.1)
- Common ion effect** the shift in an equilibrium position caused by the addition or presence of an ion involved in the equilibrium reaction. (15.1)
- Complete ionic equation** an equation that shows all substances that are strong electrolytes as ions. (4.6)
- Complex ion** a charged species consisting of a metal ion surrounded by ligands. (15.8; 21.1)
- Compound** a substance with constant composition that can be broken down into elements by chemical processes. (1.9)
- Concentration cell** a galvanic cell in which both compartments contain the same components, but at different concentrations. (17.4)
- Condensation** the process by which vapor molecules reform a liquid. (10.8)
- Condensation polymerization** a type of polymerization in which the formation of a small molecule, such as water, accompanies the extension of the polymer chain. (22.5)
- Condensation reaction** a reaction in which two molecules are joined, accompanied by the elimination of a water molecule. (20.3)
- Condensed states of matter** liquids and solids. (10.1)
- Conjugate acid** the species formed when a proton is added to a base. (14.1)
- Conjugate acid-base pair** two species related to each other by the donating and accepting of a single proton. (14.1)
- Conjugate base** what remains of an acid molecule after a proton is lost. (14.1)
- Continuous spectrum** a spectrum that exhibits all the wavelengths of visible light. (7.3)
- Control rods** rods in a nuclear reactor composed of substances that absorb neutrons. These rods regulate the power level of the reactor. (18.6)
- Coordinate covalent bond** a metal-ligand bond resulting from the interaction of a Lewis base (the ligand) and a Lewis acid (the metal ion). (21.3)
- Coordination compound** a compound composed of a complex ion and counter ions sufficient to give no net charge. (21.3)
- Coordination isomerism** isomerism in a coordination compound in which the composition of the coordination sphere of the metal ion varies. (21.4)
- Coordination number** the number of bonds formed between the metal ion and the ligands in a complex ion. (21.3)
- Copolymer** a polymer formed from the polymerization of more than one type of monomer. (22.5)
- Core electron** an inner electron in an atom; one not in the outermost (valence) principal quantum level. (7.11)
- Corrosion** the process by which metals are oxidized in the atmosphere. (17.6)
- Coulomb's law** $E = 2.31 \times 10^{-19} \left(\frac{Q_1 Q_2}{r} \right)$, where E is the energy of interaction between a pair of ions, expressed in joules; r is the distance between the ion centers in nm; and Q_1 and Q_2 are the numerical ion charges. (8.1)
- Counterions** anions or cations that balance the charge on the complex ion in a coordination compound. (21.3)
- Covalent bonding** a type of bonding in which electrons are shared by atoms. (2.6; 8.1)
- Critical mass** the mass of fissionable material required to produce a self-sustaining chain reaction. (18.6)
- Critical point** the point on a phase diagram at which the temperature and pressure have their critical values; the end point of the liquid-vapor line. (10.9)
- Critical pressure** the minimum pressure required to produce liquefaction of a substance at the critical temperature. (10.9)
- Critical reaction (nuclear)** a reaction in which exactly one neutron from each fission event causes another fission event, thus sustaining the chain reaction. (18.6)
- Critical temperature** the temperature above which vapor cannot be liquefied no matter what pressure is applied. (10.9)
- Crosslinking** the existence of bonds between adjacent chains in a polymer, thus adding strength to the material. (22.5)
- Crystal field model** a model used to explain the magnetism and colors of coordination complexes through the splitting of the d orbital energies. (21.6)
- Crystalline solid** a solid with a regular arrangement of its components. (10.3)
- Cubic closest packed (ccp) structure** a solid modeled by the closest packing of spheres with an $abcabc$ arrangement of layers; the unit cell is face-centered cubic. (10.4)
- Cyanidation** a process in which crushed gold ore is treated with an aqueous cyanide solution in the presence of air to dissolve the gold. Pure gold is recovered by reduction of the ion to the metal. (21.8)
- Cyclotron** a type of particle accelerator in which an ion introduced at the center is accelerated in an expanding spiral path by the

use of alternating electrical fields in the presence of a magnetic field. (18.3)

Cytochromes a series of iron-containing species composed of heme and a protein. Cytochromes are the principal electron-transfer molecules in the respiratory chain. (21.7)

Dalton's law of partial pressures for a mixture of gases in a container, the total pressure exerted is the sum of the pressures that each gas would exert if it were alone. (5.5)

Degenerate orbitals a group of orbitals with the same energy. (7.7)

Dehydrogenation reaction a reaction in which two hydrogen atoms are removed from adjacent carbons of a saturated hydrocarbon, giving an unsaturated hydrocarbon. (22.1)

Denaturation the breaking down of the three-dimensional structure of a protein resulting in the loss of its function. (22.6)

Denitrification the return of nitrogen from decomposed matter to the atmosphere by bacteria that change nitrates to nitrogen gas. (20.2)

Density a property of matter representing the mass per unit volume. (1.8)

Deoxyribonucleic acid (DNA) a huge nucleotide polymer having a double-helical structure with complementary bases on the two strands. Its major functions are protein synthesis and the storage and transport of genetic information. (22.6)

Desalination the removal of dissolved salts from an aqueous solution. (11.6)

Dialysis a phenomenon in which a semipermeable membrane allows transfer of both solvent molecules and small solute molecules and ions. (11.6)

Diamagnetism a type of magnetism, associated with paired electrons, that causes a substance to be repelled from the inducing magnetic field. (9.3)

Differential rate law an expression that gives the rate of a reaction as a function of concentrations; often called the rate law. (12.2)

Diffraction the scattering of light from a regular array of points or lines, producing constructive and destructive interference. (7.2)

Diffusion the mixing of gases. (5.7)

Dilution the process of adding solvent to lower the concentration of solute in a solution. (4.3)

Dimer a molecule formed by the joining of two identical monomers. (22.5)

Dipole-dipole attraction the attractive force resulting when polar molecules line up so that the positive and negative ends are close to each other. (10.1)

Dipole moment a property of a molecule whose charge distribution can be represented by a center of positive charge and a center of negative charge. (8.3)

Direct reduction furnace a furnace in which iron oxide is reduced to iron metal using milder reaction conditions than in a blast furnace. (21.8)

Disaccharide a sugar formed from two monosaccharides joined by a glycoside linkage. (22.6)

Disproportionation reaction a reaction in which a given element is both oxidized and reduced. (20.7)

Distillation a method for separating the components of a liquid mixture that depends on differences in the ease of vaporization of the components. (1.9)

Disulfide linkage an S—S bond that stabilizes the tertiary structure of many proteins. (22.6)

Double bond a bond in which two pairs of electrons are shared by two atoms. (8.8)

Downs cell a cell used for electrolyzing molten sodium chloride. (17.8)

Dry cell battery a common battery used in calculators, watches, radios, and tape players. (17.5)

Dual nature of light the statement that light exhibits both wave and particulate properties. (7.2)

Effusion the passage of a gas through a tiny orifice into an evacuated chamber. (5.7)

Electrical conductivity the ability to conduct an electric current. (4.2)

Electrochemistry the study of the interchange of chemical and electrical energy. (17)

Electrolysis a process that involves forcing a current through a cell to cause a nonspontaneous chemical reaction to occur. (17.7)

Electrolyte a material that dissolves in water to give a solution that conducts an electric current. (4.2)

Electrolytic cell a cell that uses electrical energy to produce a chemical change that would otherwise not occur spontaneously. (17.7)

Electromagnetic radiation radiant energy that exhibits wavelike behavior and travels through space at the speed of light in a vacuum. (7.1)

Electron a negatively charged particle that moves around the nucleus of an atom. (2.4)

Electron affinity the energy change associated with the addition of an electron to a gaseous atom. (7.12)

Electron capture a process in which one of the inner-orbital electrons in an atom is captured by the nucleus. (18.1)

Electron spin quantum number a quantum number representing one of the two possible values for the electron spin; either $+\frac{1}{2}$ or $-\frac{1}{2}$. (7.8)

Electronegativity the tendency of an atom in a molecule to attract shared electrons to itself. (8.2)

Element a substance that cannot be decomposed into simpler substances by chemical or physical means. (1.9)

Elementary step a reaction whose rate law can be written from its molecularity. (12.6)

$E = mc^2$ Einstein's equation proposing that energy has mass; E is energy, m is mass, and c is the speed of light. (7.2)

Empirical formula the simplest whole number ratio of atoms in a compound. (3.5)

Enantiomers isomers that are nonsuperimposable mirror images of each other. (21.4)

Endpoint the point in a titration at which the indicator changes color. (4.8)

- Endothermic** refers to a reaction where energy (as heat) flows into the system. (6.1)
- Energy** the capacity to do work or to cause heat flow. (6.1)
- Enthalpy** a property of a system equal to $E + PV$, where E is the internal energy of the system, P is the pressure of the system, and V is the volume of the system. At constant pressure the change in enthalpy equals the energy flow as heat. (6.2)
- Enthalpy (heat) of fusion** the enthalpy change that occurs to melt a solid at its melting point. (10.8)
- Entropy** a thermodynamic function that measures randomness or disorder. (16.1)
- Enzyme** a large molecule, usually a protein, that catalyzes biological reactions. (12.8)
- Equilibrium constant** the value obtained when equilibrium concentrations of the chemical species are substituted in the equilibrium expression. (13.2)
- Equilibrium expression** the expression (from the law of mass action) obtained by multiplying the product concentrations and dividing by the multiplied reactant concentrations, with each concentration raised to a power represented by the coefficient in the balanced equation. (13.2)
- Equilibrium point (thermodynamic definition)** the position where the free energy of a reaction system has its lowest possible value. (16.8)
- Equilibrium position** a particular set of equilibrium concentrations. (13.2)
- Equivalence point (stoichiometric point)** the point in a titration when enough titrant has been added to react exactly with the substance in solution being titrated. (4.9; 15.4)
- Ester** an organic compound produced by the reaction between a carboxylic acid and an alcohol. (22.4)
- Exothermic** refers to a reaction where energy (as heat) flows out of the system. (6.1)
- Exponential notation** expresses a number as $N \times 10^M$, a convenient method for representing a very large or very small number and for easily indicating the number of significant figures. (1.5)
- Faraday** a constant representing the charge on one mole of electrons; 96,485 coulombs. (17.3)
- Filtration** a method for separating the components of a mixture containing a solid and a liquid. (1.9)
- First law of thermodynamics** the energy of the universe is constant; same as the law of conservation of energy. (6.1)
- Fission** the process of using a neutron to split a heavy nucleus into two nuclei with smaller mass numbers. (18.6)
- Flotation process** a method of separating the mineral particles in an ore from the gangue that depends on the greater wettability of the mineral pieces. (21.8)
- Formal charge** the charge assigned to an atom in a molecule or polyatomic ion derived from a specific set of rules. (8.12)
- Formation constant (stability constant)** the equilibrium constant for each step of the formation of a complex ion by the addition of an individual ligand to a metal ion or complex ion in aqueous solution. (15.8)
- Fossil fuel** coal, petroleum, or natural gas; consists of carbon-based molecules derived from decomposition of once-living organisms. (6.5)
- Frasch process** the recovery of sulfur from underground deposits by melting it with hot water and forcing it to the surface by air pressure. (20.6)
- Free energy** a thermodynamic function equal to the enthalpy (H) minus the product of the entropy (S) and the Kelvin temperature (T); $G = H - TS$. Under certain conditions the change in free energy for a process is equal to the maximum useful work. (16.4)
- Free radical** a species with an unpaired electron. (22.5)
- Frequency** the number of waves (cycles) per second that pass a given point in space. (7.1)
- Fuel cell** a galvanic cell for which the reactants are continuously supplied. (17.5)
- Functional group** an atom or group of atoms in hydrocarbon derivatives that contains elements in addition to carbon and hydrogen. (22.4)
- Fusion** the process of combining two light nuclei to form a heavier, more stable nucleus. (18.6)
- Galvanic cell** a device in which chemical energy from a spontaneous redox reaction is changed to electrical energy that can be used to do work. (17.1)
- Galvanizing** a process in which steel is coated with zinc to prevent corrosion. (17.6)
- Gamma (γ) ray** a high-energy photon. (18.1)
- Gangue** the impurities (such as clay or sand) in an ore. (21.8)
- Geiger-Müller counter (Geiger counter)** an instrument that measures the rate of radioactive decay based on the ions and electrons produced as a radioactive particle passes through a gas-filled chamber. (18.4)
- Gene** a given segment of the DNA molecule that contains the code for a specific protein. (22.6)
- Geometrical (cis-trans) isomerism** isomerism in which atoms or groups of atoms can assume different positions around a rigid ring or bond. (21.4; 22.2)
- Glass** an amorphous solid obtained when silica is mixed with other compounds, heated above its melting point, and then cooled rapidly. (10.5)
- Glass electrode** an electrode for measuring pH from the potential difference that develops when it is dipped into an aqueous solution containing H^+ ions. (17.4)
- Glycosidic linkage** a $C-O-C$ bond formed between the rings of two cyclic monosaccharides by the elimination of water. (22.6)
- Graham's law of effusion** the rate of effusion of a gas is inversely proportional to the square root of the mass of its particles. (5.7)
- Greenhouse effect** a warming effect exerted by the earth's atmosphere (particularly CO_2 and H_2O) due to thermal energy retained by absorption of infrared radiation. (6.5)
- Ground state** the lowest possible energy state of an atom or molecule. (7.4)

Group (of the periodic table) a vertical column of elements having the same valence electron configuration and showing similar properties. (2.7)

Haber process the manufacture of ammonia from nitrogen and hydrogen, carried out at high pressure and high temperature with the aid of a catalyst. (3.9; 20.2)

Half-life (of a radioactive sample) the time required for the number of nuclides in a radioactive sample to reach half of the original value. (18.2)

Half-life (of a reactant) the time required for a reactant to reach half of its original concentration. (12.4)

Half-reactions the two parts of an oxidation–reduction reaction, one representing oxidation, the other reduction. (4.10; 17.1)

Halogen a Group 7A element. (2.7; 20.7)

Halogenation the addition of halogen atoms to unsaturated hydrocarbons. (22.2)

Hard water water from natural sources that contains relatively large concentrations of calcium and magnesium ions. (19.4)

Heat energy transferred between two objects due to a temperature difference between them. (6.1)

Heat capacity the amount of energy required to raise the temperature of an object by one degree Celsius. (6.2)

Heat of fusion the enthalpy change that occurs to melt a solid at its melting point. (10.8)

Heat of hydration the enthalpy change associated with placing gaseous molecules or ions in water; the sum of the energy needed to expand the solvent and the energy released from the solvent–solute interactions. (11.2)

Heat of solution the enthalpy change associated with dissolving a solute in a solvent; the sum of the energies needed to expand both solvent and solute in a solution and the energy released from the solvent–solute interactions. (11.2)

Heat of vaporization the energy required to vaporize one mole of a liquid at a pressure of one atmosphere. (10.8)

Heating curve a plot of temperature versus time for a substance where energy is added at a constant rate. (10.8)

Heisenberg uncertainty principle a principle stating that there is a fundamental limitation to how precisely both the position and momentum of a particle can be known at a given time. (7.5)

Heme an iron complex. (21.7)

Hemoglobin a biomolecule composed of four myoglobin-like units (proteins plus heme) that can bind and transport four oxygen molecules in the blood. (21.7)

Henderson–Hasselbalch equation an equation giving the relationship between the pH of an acid–base system and the concentrations of base and acid: $\text{pH} = \text{p}K_a + \log \left(\frac{[\text{base}]}{[\text{acid}]} \right)$. (15.2)

Henry's law the amount of a gas dissolved in a solution is directly proportional to the pressure of the gas above the solution. (11.3)

Hess's law in going from a particular set of reactants to a particular set of products, the enthalpy change is the same whether the reaction takes place in one step or in a series of steps; in summary, enthalpy is a state function. (6.3)

Heterogeneous equilibrium an equilibrium involving reactants and/or products in more than one phase. (13.4)

Hexagonal closest packed (hcp) structure a structure composed of closest packed spheres with an *ababab* arrangement of layers; the unit cell is hexagonal. (10.4)

Homogeneous equilibrium an equilibrium system where all reactants and products are in the same phase. (13.4)

Homopolymer a polymer formed from the polymerization of only one type of monomer. (22.5)

Hund's rule the lowest energy configuration for an atom is the one having the maximum number of unpaired electrons allowed by the Pauli exclusion principle in a particular set of degenerate orbitals, with all unpaired electrons having parallel spins. (7.11)

Hybrid orbitals a set of atomic orbitals adopted by an atom in a molecule different from those of the atom in the free state. (9.1)

Hybridization a mixing of the native orbitals on a given atom to form special atomic orbitals for bonding. (9.1)

Hydration the interaction between solute particles and water molecules. (4.1)

Hydride a binary compound containing hydrogen. The hydride ion, H^- , exists in ionic hydrides. The three classes of hydrides are covalent, interstitial, and ionic. (19.3)

Hydrocarbon a compound composed of carbon and hydrogen. (22.1)

Hydrocarbon derivative an organic molecule that contains one or more elements in addition to carbon and hydrogen. (22.4)

Hydrogen bonding unusually strong dipole–dipole attractions that occur among molecules in which hydrogen is bonded to a highly electronegative atom. (10.1)

Hydrogenation reaction a reaction in which hydrogen is added, with a catalyst present, to a carbon–carbon multiple bond. (22.2)

Hydrohalic acid an aqueous solution of a hydrogen halide. (20.7)

Hydrometallurgy a process for extracting metals from ores by use of aqueous chemical solutions. Two steps are involved: selective leaching and selective precipitation. (21.8)

Hydronium ion the H_3O^+ ion; a hydrated proton. (14.1)

Hypothesis one or more assumptions put forth to explain the observed behavior of nature. (1.2)

Ideal gas law an equation of state for a gas, where the state of the gas is its condition at a given time; expressed by $PV = nRT$, where P = pressure, V = volume, n = moles of the gas, R = the universal gas constant, and T = absolute temperature. This equation expresses behavior approached by real gases at high T and low P . (5.3)

Ideal solution a solution whose vapor pressure is directly proportional to the mole fraction of solvent present. (11.4)

Indicator a chemical that changes color and is used to mark the end point of a titration. (4.8; 15.5)

Integrated rate law an expression that shows the concentration of a reactant as a function of time. (12.2)

Interhalogen compound a compound formed by the reaction of one halogen with another. (20.7)

Intermediate a species that is neither a reactant nor a product but that is formed and consumed in the reaction sequence. (12.6)

Intermolecular forces relatively weak interactions that occur between molecules. (10.1)

Internal energy a property of a system that can be changed by a flow of work, heat or both; $\Delta E = q + w$, where ΔE is the change in the internal energy of the system, q is heat, and w is work. (6.1)

Ion an atom or a group of atoms that has a net positive or negative charge. (2.6)

Ion exchange (water softening) the process in which an ion-exchange resin removes unwanted ions (for example, Ca^{2+} and Mg^{2+}) and replaces them with Na^+ ions, which do not interfere with soap and detergent action. (19.4)

Ion pairing a phenomenon occurring in solution when oppositely charged ions aggregate and behave as a single particle. (11.7)

Ion-product (dissociation) constant (K_w) the equilibrium constant for the auto-ionization of water; $K_w = [\text{H}^+][\text{OH}^-]$. At 25°C , K_w equals 1.0×10^{-14} . (14.2)

Ion-selective electrode an electrode sensitive to the concentration of a particular ion in solution. (17.4)

Ionic bonding the electrostatic attraction between oppositely charged ions. (2.6; 8.1)

Ionic compound (binary) a compound that results when a metal reacts with a nonmetal to form a cation and an anion. (8.1)

Ionic solid (salt) a solid containing cations and anions that dissolves in water to give a solution containing the separated ions which are mobile and thus free to conduct electrical current. (2.6; 10.3)

Irreversible process any real process. When a system undergoes the changes State 1 $\rightarrow$ State 2 $\rightarrow$ State 1 by any real pathway, the universe is different than before the cyclic process took place in the system. (16.9)

Isoelectronic ions ions containing the same number of electrons. (8.4)

Isomers species with the same formula but different properties. (21.4)

Isotactic chain a polymer chain in which the substituent groups such as CH_3 are all arranged on the same side of the chain. (22.5)

Isotonic solutions solutions having identical osmotic pressures. (11.6)

Isotopes atoms of the same element (the same number of protons) with different numbers of neutrons. They have identical atomic numbers but different mass numbers. (2.5; 18)

Ketone an organic compound containing the carbonyl group



bonded to two carbon atoms. (22.4)

Kinetic energy ($\frac{1}{2}mv^2$) energy due to the motion of an object; dependent on the mass of the object and the square of its velocity. (6.1)

Kinetic molecular theory (KMT) a model that assumes that an ideal gas is composed of tiny particles (molecules) in constant motion. (5.6)

Lanthanide contraction the decrease in the atomic radii of the lanthanide series elements, going from left to right in the periodic table. (21.1)

Lanthanide series a group of 14 elements following lanthanum in the periodic table, in which the $4f$ orbitals are being filled. (7.11; 19.1; 21.1)

Lattice a three-dimensional system of points designating the positions of the centers of the components of a solid (atoms, ions, or molecules). (10.3)

Lattice energy the energy change occurring when separated gaseous ions are packed together to form an ionic solid. (8.5)

Law of conservation of energy energy can be converted from one form to another but can be neither created nor destroyed. (6.1)

Law of conservation of mass mass is neither created nor destroyed. (1.2; 2.2)

Law of definite proportion a given compound always contains exactly the same proportion of elements by mass. (2.2)

Law of mass action a general description of the equilibrium condition; it defines the equilibrium constant expression. (13.2)

Law of multiple proportions a law stating that when two elements form a series of compounds, the ratios of the masses of the second element that combine with one gram of the first element can always be reduced to small whole numbers. (2.2)

Leaching the extraction of metals from ores using aqueous chemical solutions. (21.8)

Lead storage battery a battery (used in cars) in which the anode is lead, the cathode is lead coated with lead dioxide, and the electrolyte is a sulfuric acid solution. (17.5)

Le Châtelier's principle if a change is imposed on a system at equilibrium, the position of the equilibrium will shift in a direction that tends to reduce the effect of that change. (13.7)

Lewis acid an electron-pair acceptor. (14.11)

Lewis base an electron-pair donor. (14.11)

Lewis structure a diagram of a molecule showing how the valence electrons are arranged among the atoms in the molecule. (8.10)

Ligand a neutral molecule or ion having a lone pair of electrons that can be used to form a bond to a metal ion; a Lewis base. (21.3)

Lime-soda process a water-softening method in which lime and soda ash are added to water to remove calcium and magnesium ions by precipitation. (14.6)

Limiting reactant (limiting reagent) the reactant that is completely consumed when a reaction is run to completion. (3.9)

Line spectrum a spectrum showing only certain discrete wavelengths. (7.3)

Linear accelerator a type of particle accelerator in which a changing electrical field is used to accelerate a positive ion along a linear path. (18.3)

Linkage isomerism isomerism involving a complex ion where the ligands are all the same but the point of attachment of at least one of the ligands differs. (21.4)

Liquefaction the transformation of a gas into a liquid. (19.1)

Localized electron (LE) model a model which assumes that a molecule is composed of atoms that are bound together by sharing pairs of electrons using the atomic orbitals of the bound atoms. (8.9)

London dispersion forces the forces, existing among noble gas atoms and nonpolar molecules, that involve an accidental dipole that induces a momentary dipole in a neighbor. (10.1)

Lone pair an electron pair that is localized on a given atom; an electron pair not involved in bonding. (8.9)

Magnetic quantum number m_ℓ , the quantum number relating to the orientation of an orbital in space relative to the other orbitals with the same ℓ quantum number. It can have integral values between ℓ and $-\ell$, including zero. (7.6)

Main-group (representative) elements elements in the groups labeled 1A, 2A, 3A, 4A, 5A, 6A, 7A, and 8A in the periodic table. The group number gives the sum of the valence s and p electrons. (7.11; 18.1)

Major species the components present in relatively large amounts in a solution. (14.3)

Manometer a device for measuring the pressure of a gas in a container. (5.1)

Mass the quantity of matter in an object. (1.3)

Mass defect the change in mass occurring when a nucleus is formed from its component nucleons. (18.5)

Mass number the total number of protons and neutrons in the atomic nucleus of an atom. (2.5; 18)

Mass percent the percent by mass of a component of a mixture (11.1) or of a given element in a compound. (3.4)

Mass spectrometer an instrument used to determine the relative masses of atoms by the deflection of their ions on a magnetic field. (3.1)

Matter the material of the universe. (1.9)

Messenger RNA (mRNA) a special RNA molecule built in the cell nucleus that migrates into the cytoplasm and participates in protein synthesis. (22.6)

Metal an element that gives up electrons relatively easily and is lustrous, malleable, and a good conductor of heat and electricity. (2.7)

Metalloids (semimetals) elements along the division line in the periodic table between metals and nonmetals. These elements exhibit both metallic and nonmetallic properties. (7.13; 19.1)

Metallurgy the process of separating a metal from its ore and preparing it for use. (19.1; 21.8)

Millimeters of mercury (mmHg) a unit of pressure, also called a torr, $760 \text{ mm Hg} = 760 \text{ torr} = 101,325 \text{ Pa} = 1 \text{ standard atmosphere}$. (5.1)

Mineral a relatively pure compound as found in nature. (21.8)

Model (theory) a set of assumptions put forth to explain the observed behavior of matter. The models of chemistry usually involve assumptions about the behavior of individual atoms or molecules. (1.2)

Moderator a substance used in a nuclear reactor to slow down the neutrons. (18.6)

Molal boiling-point elevation constant a constant characteristic of a particular solvent that gives the change in boiling point as a function of solution molality; used in molecular weight determinations. (11.5)

Molal freezing-point depression constant a constant characteristic of a particular solvent that gives the change in freezing point as a function of the solution molality; used in molecular weight determinations (11.5)

Molality the number of moles of solute per kilogram of solvent in a solution. (11.1)

Molar heat capacity the energy required to raise the temperature of one mole of a substance by one degree Celsius. (6.2)

Molar mass the mass in grams of one mole of molecules or formula units of a substance; also called *molecular weight*. (3.3)

Molar volume the volume of one mole of an ideal gas; equal to 22.42 liters at STP. (5.4)

Molarity moles of solute per volume of solution in liters. (4.3; 11.1)

Mole (mol) the number equal to the number of carbon atoms in exactly 12 grams of pure ^{12}C ; Avogadro's number. One mole represents 6.022×10^{23} units. (3.2)

Mole fraction the ratio of the number of moles of a given component in a mixture to the total number of moles in the mixture. (5.5; 11.1)

Mole ratio (stoichiometry) the ratio of moles of one substance to moles of another substance in a balanced chemical equation. (3.8)

Molecular equation an equation representing a reaction in solution showing the reactants and products in undissociated form, whether they are strong or weak electrolytes. (4.6)

Molecular formula the exact formula of a molecule, giving the types of atoms and the number of each type. (3.5)

Molecular orbital (MO) model a model that regards a molecule as a collection of nuclei and electrons, where the electrons are assumed to occupy orbitals much as they do in atoms, but having the orbitals extend over the entire molecule. In this model the electrons are assumed to be delocalized rather than always located between a given pair of atoms. (9.2; 10.4)

Molecular orientations (kinetics) orientations of molecules during collisions, some of which can lead to reaction while others cannot. (12.7)

Molecular solid a solid composed of neutral molecules at the lattice points. (10.3)

Molecular structure the three-dimensional arrangement of atoms in a molecule. (8.13)

Molecularity the number of species that must collide to produce the reaction represented by an elementary step in a reaction mechanism. (12.6)

Molecule a bonded collection of two or more atoms of the same or different elements. (2.6)

Monodentate (unidentate) ligand a ligand that can form one bond to a metal ion. (21.3)

Monoprotic acid an acid with one acidic proton. (14.2)

Monosaccharide (simple sugar) a polyhydroxy ketone or aldehyde containing from three to nine carbon atoms. (22.6)

Myoglobin an oxygen-storing biomolecule consisting of a heme complex and a proton. (21.7)

Natural law a statement that expresses generally observed behavior. (1.2)

Nernst equation an equation relating the potential of an electrochemical cell to the concentrations of the cell components:

$$\mathcal{E} = \mathcal{E}^\circ - \frac{0.0591}{n} \log(Q) \text{ at } 25^\circ\text{C} \quad (17.4)$$

Net ionic equation an equation for a reaction in solution, where strong electrolytes are written as ions, showing only those components that are directly involved in the chemical change. (4.6)

Network solid an atomic solid containing strong directional covalent bonds. (10.5)

Neutralization reaction an acid–base reaction. (4.8)

Neutron a particle in the atomic nucleus with mass virtually equal to the proton's but with no charge. (2.5; 18)

Nitrogen cycle the conversion of N_2 to nitrogen-containing compounds, followed by the return of nitrogen gas to the atmosphere by natural decay processes. (20.2)

Nitrogen fixation the process of transforming N_2 to nitrogen-containing compounds useful to plants. (20.2)

Nitrogen-fixing bacteria bacteria in the root nodules of plants that can convert atmospheric nitrogen to ammonia and other nitrogen-containing compounds useful to plants. (20.2)

Noble gas a Group 8A element. (2.7; 20.8)

Node an area of an orbital having zero electron probability. (7.7)

Nonelectrolyte a substance that, when dissolved in water, gives a nonconducting solution. (4.2)

Nonmetal an element not exhibiting metallic characteristics. Chemically, a typical nonmetal accepts electrons from a metal. (2.7)

Normal boiling point the temperature at which the vapor pressure of a liquid is exactly one atmosphere. (10.8)

Normal melting point the temperature at which the solid and liquid states have the same vapor pressure under conditions where the total pressure on the system is one atmosphere. (10.8)

Normality the number of equivalents of a substance dissolved in a liter of solution. (11.1)

Nuclear atom an atom having a dense center of positive charge (the nucleus) with electrons moving around the outside. (2.4)

Nuclear transformation the change of one element into another. (18.3)

Nucleon a particle in an atomic nucleus, either a neutron or a proton. (18)

Nucleotide a monomer of the nucleic acids composed of a five-carbon sugar, a nitrogen-containing base, and phosphoric acid. (22.6)

Nucleus the small, dense center of positive charge in an atom. (2.4)

Nuclide the general term applied to each unique atom; represented by ${}^A_Z\text{X}$, where X is the symbol for a particular element. (18)

Octet rule the observation that atoms of nonmetals tend to form the most stable molecules when they are surrounded by eight electrons (to fill their valence orbitals). (8.10)

Open hearth process a process for producing steel by oxidizing and removing the impurities in molten iron using external heat and a blast of air or oxygen. (21.8)

Optical isomerism isomerism in which the isomers have opposite effects on plane-polarized light. (21.4)

Orbital a specific wave function for an electron in an atom. The square of this function gives the probability distribution for the electron. (7.5)

d-Orbital splitting a splitting of the d orbitals of the metal ion in a complex such that the orbitals pointing at the ligands have higher energies than those pointing between the ligands. (21.6)

Order (of reactant) the positive or negative exponent, determined by experiment, of the reactant concentration in a rate law. (12.2)

Organic acid an acid with a carbon-atom backbone; often contains the carboxyl group. (14.2)

Organic chemistry the study of carbon-containing compounds (typically chains of carbon atoms) and their properties. (22)

Osmosis the flow of solvent into a solution through a semipermeable membrane. (11.6)

Osmotic pressure (π) the pressure that must be applied to a solution to stop osmosis; $\pi = MRT$. (11.6)

Ostwald process a commercial process for producing nitric acid by the oxidation of ammonia. (20.2)

Oxidation an increase in oxidation state (a loss of electrons). (4.9; 17.1)

Oxidation–reduction (redox) reaction a reaction in which one or more electrons are transferred. (4.9; 17.1)

Oxidation states a concept that provides a way to keep track of electrons in oxidation–reduction reactions according to certain rules. (4.9; 21.3)

Oxidizing agent (electron acceptor) a reactant that accepts electrons from another reactant. (4.9; 17.1)

Oxyacid an acid in which the acidic proton is attached to an oxygen atom. (14.2)

Ozone O_3 , the form of elemental oxygen in addition to the much more common O_2 . (20.5)

Paramagnetism a type of induced magnetism, associated with unpaired electrons, that causes a substance to be attracted to the inducing magnetic field. (9.3)

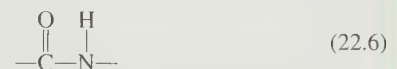
Partial pressures the independent pressures exerted by different gases in a mixture. (5.5)

Particle accelerator a device used to accelerate nuclear particles to very high speeds. (18.3)

Pascal the SI unit of pressure; equal to newtons per meter squared. (5.1)

Pauli exclusion principle in a given atom no two electrons can have the same set of four quantum numbers. (7.8)

Peptide linkage the bond resulting from the condensation reaction between amino acids; represented by:



Percent dissociation the ratio of the amount of a substance that is dissociated at equilibrium to the initial concentration of the substance in a solution, multiplied by 100. (14.5)

Percent yield the actual yield of a product as a percentage of the theoretical yield. (3.9)

Periodic table a chart showing all the elements arranged in columns with similar chemical properties. (2.7)

pH curve (titration curve) a plot showing the pH of a solution being analyzed as a function of the amount of titrant added. (15.4)

pH scale a log scale based on 10 and equal to $-\log[H^+]$; a convenient way to represent solution acidity. (14.3)

Phase diagram a convenient way of representing the phases of a substance in a closed system as a function of temperature and pressure. (10.9)

Phenyl group the benzene molecule minus one hydrogen atom. (22.3)

Photochemical smog air pollution produced by the action of light on oxygen, nitrogen oxides, and unburned fuel from auto exhaust to form ozone and other pollutants. (5.9)

Photon a quantum of electromagnetic radiation. (7.2)

Physical change a change in the form of a substance, but not in its chemical composition; chemical bonds are not broken in a physical change. (1.9)

Pi (π) bond a covalent bond in which parallel p orbitals share an electron pair occupying the space above and below the line joining the atoms. (9.1)

Planck's constant the constant relating the change in energy for a system to the frequency of the electromagnetic radiation absorbed or emitted; equal to 6.626×10^{-34} J s. (7.2)

Polar covalent bond a covalent bond in which the electrons are not shared equally because one atom attracts them more strongly than the other. (8.1)

Polar molecule a molecule that has a permanent dipole moment. (4.1)

Polyatomic ion an ion containing a number of atoms. (2.6)

Polyelectronic atom an atom with more than one electron. (7.9)

Polymer a large, usually chainlike molecule built from many small molecules (monomers). (22.5)

Polymerization a process in which many small molecules (monomers) are joined together to form a large molecule. (22.2)

Polypeptide a polymer formed from amino acids joined together by peptide linkages. (22.6)

Polyprotic acid an acid with more than one acidic proton. It dissociates in a stepwise manner, one proton at a time. (14.7)

Porous disk a disk in a tube connecting two different solutions in a galvanic cell that allows ion flow without extensive mixing of the solutions. (17.1)

Porphyrin a planar ligand with a central ring structure and various substituent groups at the edges of the ring. (21.7)

Positional probability a type of probability that depends on the number of arrangements in space that yield a particular state. (16.1)

Positron production a mode of nuclear decay in which a particle is formed having the same mass as an electron but opposite charge. The net effect is to change a proton to a neutron. (18.1)

Potential energy energy due to position or composition. (6.1)

Precipitation reaction a reaction in which an insoluble substance forms and separates from the solution. (4.5)

Precision the degree of agreement among several measurements of the same quantity; the reproducibility of a measurement. (1.4)

Primary structure (of a protein) the order (sequence) of amino acids in the protein chain. (22.6)

Principal quantum number (n) the quantum number relating to the size and energy of an orbital; it can have any positive integer value. (7.6)

Probability distribution the square of the wave function indicating the probability of finding an electron at a particular point in space. (7.5)

Product a substance resulting from a chemical reaction. It is shown to the right of the arrow in a chemical equation. (3.6)

Protein a natural high-molecular-weight polymer formed by condensation reactions between amino acids. (22.6)

Proton a positively charged particle in an atomic nucleus. (2.5; 18)

Pure substance a substance with constant composition. (1.9)

Pyrometallurgy recovery of a metal from its ore by treatment at high temperatures. (21.8)

Quantization the concept that energy can occur only in discrete units called *quanta*. (7.2)

Rad a unit of radiation dosage corresponding to 10^{-2} J of energy deposited per kilogram of tissue (from radiation absorbed dose). (18.7)

Radioactive decay (radioactivity) the spontaneous decomposition of a nucleus to form a different nucleus. (2.4; 18.1)

Radiocarbon dating (carbon-14 dating) a method for dating ancient wood or cloth based on the rate of radioactive decay of the nuclide ^{14}C . (18.4)

Radiotracer a radioactive nuclide, introduced into an organism for diagnostic purposes, whose pathway can be traced by monitoring its radioactivity. (18.4)

Random error an error that has an equal probability of being high or low. (1.4)

Raoult's law the vapor pressure of a solution is directly proportional to the mole fraction of solvent present. (11.4)

Rate constant the proportionality constant in the relationship between reaction rate and reactant concentrations. (12.2)

Rate of decay the change in the number of radioactive nuclides in a sample per unit time. (18.2)

Rate-determining step the slowest step in a reaction mechanism, the one determining the overall rate. (12.6)

Rate law (differential rate law) an expression that shows how the rate of reaction depends on the concentration of reactants. (12.2)

Reactant a starting substance in a chemical reaction. It appears to the left of the arrow in a chemical equation. (3.6)

Reaction mechanism the series of elementary steps involved in a chemical reaction. (12.6)

Reaction quotient Q a quotient obtained by applying the law of mass action to initial concentrations rather than to equilibrium concentrations. (13.5)

- Reaction rate** the change in concentration of a reactant or product per unit time. (12.1)
- Reactor core** the part of a nuclear reactor where the fission reaction takes place. (18.6)
- Reducing agent (electron donor)** a reactant that donates electrons to another substance to reduce the oxidation state of one of its atoms. (4.9; 17.1)
- Reduction** a decrease in oxidation state (a gain of electrons). (4.9; 17.1)
- Rem** a unit of radiation dosage that accounts for both the energy of the dose and its effectiveness in causing biological damage (from roentgen equivalent for man). (18.7)
- Resonance** a condition occurring when more than one valid Lewis structure can be written for a particular molecule. The actual electronic structure is not represented by any one of the Lewis structures but by the average of all of them. (8.12)
- Reverse osmosis** the process occurring when the external pressure on a solution causes a net flow of solvent through a semipermeable membrane from the solution to the solvent. (11.6)
- Reversible process** a cyclic process carried out by a hypothetical pathway, which leaves the universe exactly the same as it was before the process. No real process is reversible. (16.9)
- Ribonucleic acid (RNA)** a nucleotide polymer that transmits the genetic information stored in DNA to the ribosomes for protein synthesis. (22.6)
- Roasting** a process of converting sulfide minerals to oxides by heating in air at temperatures below their melting points. (21.8)
- Root mean square velocity** the square root of the average of the squares of the individual velocities of gas particles. (5.6)
- Salt** an ionic compound. (14.8)
- Salt bridge** a U-tube containing an electrolyte that connects the two compartments of a galvanic cell, allowing ion flow without extensive mixing of the different solutions. (17.1)
- Scientific method** the process of studying natural phenomena, involving observations, forming laws and theories, and testing of theories by experimentation. (1.1)
- Scintillation counter** an instrument that measures radioactive decay by sensing the flashes of light produced in a substance by the radiation. (18.4)
- Second law of thermodynamics** in any spontaneous process, there is always an increase in the entropy of the universe. (16.2)
- Secondary structure (of a protein)** the three-dimensional structure of the protein chain (for example, α -helix, random coil, or pleated sheet). (22.6)
- Selective precipitation** a method of separating metal ions from an aqueous mixture by using a reagent whose anion forms a precipitate with only one or a few of the ions in the mixture. (4.7; 15.7)
- Semiconductor** a substance conducting only a slight electrical current at room temperature, but showing increased conductivity at higher temperatures. (10.5)
- Semipermeable membrane** a membrane that allows solvent but not solute molecules to pass through. (11.6)
- SI system** International System of units based on the metric system and units derived from the metric system. (1.2)
- Side chain (of amino acid)** the hydrocarbon group on an amino acid represented by H, CH_3 , or a more complex substituent. (22.6)
- Sigma (σ) bond** a covalent bond in which the electron pair is shared in an area centered on a line running between the atoms. (9.1)
- Significant figures** the certain digits and the first uncertain digit of a measurement. (1.4)
- Silica** the fundamental silicon-oxygen compound, which has the empirical formula SiO_2 , and forms the basis of quartz and certain types of sand. (10.5)
- Silicates** salts that contain metal cations and polyatomic silicon-oxygen anions that are usually polymeric. (10.5)
- Single bond** a bond in which one pair of electrons is shared by two atoms. (8.8)
- Smelting** a metallurgical process that involves reducing metal ions to the free metal. (21.8)
- Solubility** the amount of a substance that dissolves in a given volume of solvent at a given temperature. (4.2)
- Solubility product constant** the constant for the equilibrium expression representing the dissolving of an ionic solid in water. (15.6)
- Solute** a substance dissolved in a liquid to form a solution. (4.2; 11.1)
- Solution** a homogeneous mixture. (1.9)
- Solvent** the dissolving medium in a solution. (4.2)
- Somatic damage** radioactive damage to an organism resulting in its sickness or death. (18.7)
- Space-filling model** a model of a molecule showing the relative sizes of the atoms and their relative orientations. (2.6)
- Specific heat capacity** the energy required to raise the temperature of one gram of a substance by one degree Celsius. (6.2)
- Spectator ions** ions present in solution that do not participate directly in a reaction. (4.6)
- Spectrochemical series** a listing of ligands in order based on their ability to produce d -orbital splitting. (21.6)
- Spontaneous fission** the spontaneous splitting of a heavy nuclide into two lighter nuclides. (18.1)
- Spontaneous process** a process that occurs without outside intervention. (16.1)
- Standard atmosphere** a unit of pressure equal to 760 mm Hg. (5.1)
- Standard enthalpy of formation** the enthalpy change that accompanies the formation of one mole of a compound at 25°C from its elements, with all substances in their standard states at that temperature. (6.4)
- Standard free energy change** the change in free energy that will occur for one unit of reaction if the reactants in their standard states are converted to products in their standard states. (16.6)
- Standard free energy of formation** the change in free energy that accompanies the formation of one mole of a substance from its constituent elements with all reactants and products in their standard states. (16.6)

Standard hydrogen electrode a platinum conductor in contact with 1 M H^+ ions and bathed by hydrogen gas at one atmosphere. (17.2)

Standard reduction potential the potential of a half-reaction under standard state conditions, as measured against the potential of the standard hydrogen electrode. (17.2)

Standard solution a solution whose concentration is accurately known. (4.3)

Standard state a reference state for a specific substance defined according to a set of conventional definitions. (6.4)

Standard temperature and pressure (STP) the condition $0^\circ C$ and 1 atmosphere of pressure. (5.4)

Standing wave a stationary wave as on a string of a musical instrument; in the wave mechanical model, the electron in the hydrogen atom is considered to be a standing wave. (7.5)

State function (property) a property that is independent of the pathway. (6.1)

States of matter the three different forms in which matter can exist; solid, liquid, and gas. (1.9)

Stereoisomerism isomerism in which all the bonds in the isomers are the same but the spatial arrangements of the atoms are different. (21.4)

Steric factor the factor (always less than 1) that reflects the fraction of collisions with orientations that can produce a chemical reaction. (12.7)

Stoichiometric quantities quantities of reactants mixed in exactly the correct amounts so that all are used up at the same time. (3.9)

Strong acid an acid that completely dissociates to produce an H^+ ion and the conjugate base. (4.2; 14.2)

Strong base a metal hydroxide salt that completely dissociates into its ions in water. (4.2; 14.6)

Strong electrolyte a material that, when dissolved in water, gives a solution that conducts an electric current very efficiently. (4.2)

Structural formula the representation of a molecule in which the relative positions of the atoms are shown and the bonds are indicated by lines. (2.6)

Structural isomerism isomerism in which the isomers contain the same atoms but one or more bonds differ. (21.4; 22.1)

Subcritical reaction (nuclear) a reaction in which less than one neutron causes another fission event and the process dies out. (18.6)

Sublimation the process by which a substance goes directly from the solid to the gaseous state without passing through the liquid state. (10.8)

Subshell a set of orbitals with a given azimuthal quantum number. (7.6)

Substitution reaction (hydrocarbons) a reaction in which an atom, usually a halogen, replaces a hydrogen atom in a hydrocarbon. (22.1)

Supercooling the process of cooling a liquid below its freezing point without its changing to a solid. (10.8)

Supercritical reaction (nuclear) a reaction in which more than one neutron from each fission event causes another fission event. The process rapidly escalates to a violent explosion. (18.6)

Superheating the process of heating a liquid above its boiling point without its boiling. (10.8)

Superoxide a compound containing the O_2^- anion. (19.2)

Surface tension the resistance of a liquid to an increase in its surface area. (10.2)

Surroundings everything in the universe surrounding a thermodynamic system. (6.1)

Syndiotactic chain a polymer chain in which the substituent groups such as CH_3 are arranged on alternate sides of the chain. (22.5)

Syngas synthetic gas, a mixture of carbon monoxide and hydrogen, obtained by coal gasification. (6.6)

System (thermodynamic) that part of the universe on which attention is to be focused. (6.1)

Systematic error an error that always occurs in the same direction. (1.4)

Tempering a process in steel production that fine-tunes the proportions of carbon crystals and cementite by heating to intermediate temperatures followed by rapid cooling. (21.8)

Termolecular step a reaction involving the simultaneous collision of three molecules. (12.6)

Tertiary structure (of a protein) the overall shape of a protein, long and narrow or globular, maintained by different types of intramolecular interactions. (22.6)

Theoretical yield the maximum amount of a given product that can be formed when the limiting reactant is completely consumed. (3.9)

Theory a set of assumptions put forth to explain some aspect of the observed behavior of matter. (1.2)

Thermal pollution the oxygen-depleting effect on lakes and rivers of using water for industrial cooling and returning it to its natural source at a higher temperature. (11.3)

Thermodynamic stability (nuclear) the potential energy of a particular nucleus as compared to the sum of the potential energies of its component protons and neutrons. (18.1)

Thermodynamics the study of energy and its interconversions. (6.1)

Thermoplastic polymer a substance that when molded to a certain shape under appropriate conditions can later be remelted. (22.5)

Thermoset polymer a substance that when molded to a certain shape under pressure and high temperatures cannot be softened again or dissolved. (22.5)

Third law of thermodynamics the entropy of a perfect crystal at 0 K is zero. (16.5)

Titration a technique in which one solution is used to analyze another. (4.8)

Torr another name for millimeter of mercury (mm Hg). (5.1)

Transfer RNA (tRNA) a small RNA fragment that finds specific amino acids and attaches them to the protein chain as dictated by the codons in mRNA. (22.6)

Transition metals several series of elements in which inner orbitals (d or f orbitals) are being filled. (7.11; 19.1)

Transuranium elements the elements beyond uranium that are made artificially by particle bombardment. (18.3)

Triple bond a bond in which three pairs of electrons are shared by two atoms. (8.8)

Triple point the point on a phase diagram at which all three states of a substance are present. (10.9)

Tyndall effect the scattering of light by particles in a suspension. (11.8)

Uncertainty (in measurement) the characteristic that any measurement involves estimates and cannot be exactly reproduced. (1.4)

Unimolecular step a reaction step involving only one molecule. (12.6)

Unit cell the smallest repeating unit of a lattice. (10.3)

Unit factor method an equivalence statement between units used for converting from one unit to another. (1.6)

Universal gas constant the combined proportionality constant in the ideal gas law; $0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol}$ or $8.3145 \text{ J/K} \cdot \text{mol}$. (5.3)

Valence electrons the electrons in the outermost principal quantum level of an atom. (7.11)

Valence shell electron-pair repulsion (VSEPR) model a model whose main postulate is that the structure around a given atom in a molecule is determined principally by minimizing electron-pair repulsions. (8.13)

Van der Waals equation a mathematical expression for describing the behavior of real gases. (5.8)

Van't Hoff factor the ratio of moles of particles in solution to moles of solute dissolved. (11.7)

Vapor pressure the pressure of the vapor over a liquid at equilibrium. (10.8)

Vaporization (evaporization) the change in state that occurs when a liquid evaporates to form a gas. (10.8)

Viscosity the resistance of a liquid to flow. (10.2)

Volt the unit of electrical potential defined as one joule of work per coulomb of charge transferred. (17.1)

Voltmeter an instrument that measures cell potential by drawing electric current through a known resistance. (17.1)

Volumetric analysis a process involving titration of one solution with another. (4.8)

Vulcanization a process in which sulfur is added to rubber and the mixture is heated, causing crosslinking of the polymer chains and thus adding strength to the rubber. (22.5)

Wave function a function of the coordinates of an electron's position in three-dimensional space that describes the properties of the electron. (7.5)

Wave mechanical model a model for the hydrogen atom in which the electron is assumed to behave as a standing wave. (7.5)

Wavelength the distance between two consecutive peaks or troughs in a wave. (7.1)

Weak acid an acid that dissociates only slightly in aqueous solution. (4.2; 14.2)

Weak base a base that reacts with water to produce hydroxide ions to only a slight extent in aqueous solution. (4.2; 14.6)

Weak electrolyte a material which, when dissolved in water, gives a solution that conducts only a small electric current. (4.2)

Weight the force exerted on an object by gravity. (1.3)

Work force acting over a distance. (6.1)

X-ray diffraction a technique for establishing the structure of crystalline solids by directing X rays of a single wavelength at a crystal and obtaining a diffraction pattern from which interatomic spaces can be determined. (10.3)

Zone of nuclear stability the area encompassing the stable nuclides on a plot of their positions as a function of the number of protons and the number of neutrons in the nucleus. (18.1)

Zone refining a metallurgical process for obtaining a highly pure metal that depends on continuously melting the impure material and recrystallizing the pure metal. (21.8)

Answers to Selected Exercises

The answers listed here are from the *Complete Solutions Guide*, in which rounding is carried out at each intermediate step in a calculation in order to show the correct number of significant figures for that step. Therefore, an answer given here may differ in the last digit from the result obtained by carrying extra digits throughout the entire calculation and rounding at the end (the procedure you should follow).

Chapter 1

17. No, it is useful whenever a systematic approach of observation and hypothesis testing can be used. **19.** Volume readings are estimated to one decimal place past the markings on the glassware. The assumed uncertainty is ± 1 in the estimated digit. **a.** The volume would be estimated to the tenths place since the markings are to ones place. A sample reading would be 4.2 with an uncertainty of ± 0.1 . This reading has two significant figures. **b.** 10.52 ± 0.01 would be a sample reading and the uncertainty; this reading has four significant figures. **c.** 18 ± 1 would be a sample reading and uncertainty, with the reading having two significant figures. **21.** Chemical changes involve the making and breaking of chemical forces (bonds). Physical changes do not. The identity of a substance changes after a chemical change, but not after a physical change. **23. a.** Inexact; **b.** Exact; **c.** Exact; $36 \text{ in/yd} \times 2.54 \text{ cm/in} \times 1 \text{ m/100 cm} = 0.9144 \text{ m/yd}$ (All conversion factors used are exact.) **d.** Inexact; the announced attendance is generally the number of tickets sold, not the number who were actually in the stadium. Some people who paid may not have gone, some may sneak in without paying, etc. **e.** Exact; **f.** Inexact **25. a.** 2; **b.** 4; **c.** 4; **d.** 4; **e.** 3; **f.** 3; **g.** 4; **h.** 7 **27. a.** 3.13×10^2 ; **b.** 3.13×10^{-4} ; **c.** 3.13×10^7 ; **d.** 3.13×10^{-1} ; **e.** 3.13×10^{-2} . **29. a.** 102.623; **b.** 236.2; **c.** 3.0814; **d.** 4.67 **31. a.** 467; **b.** 0.24; **c.** 33.04; **d.** 75; **e.** 0.12; **f.** 0.21; **g.** 4.9; **h.** 0.01 **33. a.** 84.3 mm; **b.** 2.41 m; **c.** $2.945 \times 10^{-5} \text{ cm}$; **d.** 14.45 km; **e.** $2.353 \times 10^5 \text{ mm}$; **f.** $0.9033 \mu\text{m}$ **35. a.** 8 lb and 9.9 oz; $20\frac{1}{2} \text{ in}$; **b.** $4.0 \times 10^4 \text{ km}$, $4.0 \times 10^7 \text{ m}$; **c.** $1.2 \times 10^{-2} \text{ m}^3$, 12 L , 730 in^3 , 0.42 ft^3 **37. a.** $4.00 \times 10^2 \text{ rods}$; 10.0 furlongs ; $2.01 \times 10^3 \text{ m}$; 2.01 km ; **b.** 8390.0 rods; 209.75 furlongs; 42,195 m; 42.195 km **39. a.** 0.373 kg, 0.822 lb; **b.** 31.1 g, 156 carats; **c.** 19.3 cm^3 **41.** $2.95 \times 10^9 \text{ knots}$ **43.** The spouse's car, with 33 mi/gal, has the better gas mileage. **45.** \$1.59 **47.** 39.2°C , 312.4 K **49. a.** 351.3 K ; 173°F ; **b.** 248 K ; -13°F ; **c.** 0 K ; -459°F ; **d.** 1074 K ; 1470°F **51.** $69.1 \pm 0.2^\circ\text{F}$ **53.** $2.70 \times 10^3 \text{ kg/m}^3$, 169 lb/ft^3 **55.** $1 \times 10^6 \text{ g/cm}^3$ **57.** 0.28 cm^3 **59.** 3.8 g/cm^3 **61. a.** Both are the same mass; **b.** 1.0 mL mercury; **c.** Both are the same mass; **d.** 1.0 L benzene **63.** 2.77 cm **65.** Solid: own volume, own shape, does not flow. Liquid: own volume, takes shape of container, flows. Gas: takes volume and shape of container, flows **67. a.** Picture iv represents a gaseous compound. Pictures ii and iii also contain a gaseous compound but have a gaseous element present. **b.** Picture vi represents a mixture of two elemental gases. **c.** Picture v represents a solid element. **d.** Pictures ii and iii both represent a mixture of a gaseous element and a gaseous compound. **69. a.** physical; **b.** chemical; **c.** physical; **d.** chemical **71.** $6.02 \times 10^{17} \text{ atoms}$; $2.08 \times 10^{-4} \text{ mol}$ **73.** $1.0 \times 10^5 \text{ bags}$ **75.** $7 \times 10^5 \text{ kg}$ **77. a.** Volume $\times$ density = mass; the orange block is more dense. Since mass (orange) $>$ mass (blue) and volume (orange) $<$ volume (blue), then the density of the orange block must be greater to account for the larger mass of the orange block. **b.** Which block is more dense cannot be determined. Since mass (orange) $>$ mass (blue) and volume (orange) $>$ volume (blue), then the density of the orange block may or may not be larger than the blue block. If the blue block is more dense,

then its density cannot be so large that the mass of the smaller blue block becomes larger than the orange block mass. **c.** The blue block is more dense. Since mass (blue) = mass (orange) and volume (blue) $<$ volume (orange), then the density of the blue block must be larger to equate the masses. **d.** The blue block is more dense. Since mass (blue) $>$ mass (orange) and the volumes are equal, then the density of the blue block must be larger to give the blue block the larger mass. **79.** $8.5 \pm 0.5 \text{ g/cm}^3$ **81.** In a subtraction, the result gets smaller, but the uncertainties are added. If the two numbers are very close, the uncertainty may be larger than the result. **83.** $d_{\text{old}} = 8.8 \text{ g/cm}^3$, $d_{\text{new}} = 7.17 \text{ g/cm}^3$; $d_{\text{new}}/d_{\text{old}} = \text{mass}_{\text{new}}/\text{mass}_{\text{old}} = 0.81$; The difference in mass is accounted for by the difference in the alloy used (if the assumptions are correct). **85. a.** One possibility is that rope B is not attached to anything and rope A and rope C are connected via a pair of pulleys and/or gears; **b.** Try to pull rope B out of the box. Measure the distance moved by C for a given movement of A. Hold either A or C firmly while pulling on the other rope.

Chapter 2

15. a. Atoms have mass and are neither destroyed nor created by chemical reactions. Therefore, mass is neither created nor destroyed by chemical reactions. Mass is conserved. **b.** The composition of a substance depends on the number and kinds of atoms that form it. **c.** Compounds of the same elements differ only in the numbers of atoms of the elements forming them, i.e., NO, N₂O, NO₂. **17.** Deflection of cathode rays by magnetic and electric fields led to the conclusion that they were negatively charged. The cathode ray was produced at the negative electrode and repelled by the negative pole of the applied electric field. **19.** The proton and the neutron have similar mass, with the mass of the neutron being slightly larger than that of the proton. Each of these particles has a mass approximately 1800 times greater than that of an electron. The combination of the protons and the neutrons in the nucleus make up the bulk of the mass of an atom, but the electrons make the greatest contribution to the chemical properties of the atom. **21.** The atomic number of an element is equal to the number of protons in the nucleus of an atom of that element. The mass number is the sum of the number of protons and neutrons in the nucleus. The atomic mass is the actual mass of a particular isotope (including electrons). As we will see in Chapter 3, the average mass of an atom is taken from a measurement made on a large number of atoms. The average atomic mass value is listed in the periodic table. **23.** A compound will always contain the same numbers (and types) of atoms. A given amount of hydrogen will react only with a specific amount of oxygen. Any excess oxygen will remain unreacted. **25. a.** The composition of a substance depends on the number of atoms of each element making up the compound (depends on the formula of the compound) and not on the composition of the mixture from which it was formed. **b.** Avogadro's hypothesis implies that volume ratios are equal to molecule ratios at constant temperature and pressure. $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2 \text{ HCl}(\text{g})$; from the balanced equation, the volume of HCl produced will be twice the volume of H₂ (or Cl₂) reacted. **27.** The F-to-S mass ratios are simple whole numbers, 1:2:3. **29.** O, 7.94; Na, 22.8; Mg, 11.9; O and Mg are incorrect by a factor of ≈ 2 ; correct formulas are H₂O, Na₂O, and MgO. **31.** Using $r = 5 \times 10^{-14} \text{ cm}$, $d_{\text{nucleus}} = 3 \times 10^{15} \text{ g/cm}^3$; using $r = 1 \times 10^{-8} \text{ cm}$, $d_{\text{atom}} = 0.4 \text{ g/cm}^3$ **33.** 37 **35.** sodium, Na; beryllium, Be; manganese, Mn; chromium, Cr; uranium, U **37.** Sn: tin, Pt: platinum, Co: cobalt, Ni: nickel, Mg: magnesium, Ba: barium, K: potassium. **39.** The noble gases are He, Ne, Ar,

Kr, Xe, and Rn (helium, neon, argon, krypton, xenon, and radon). All isotopes of radon are radioactive. **41.** a. 8; b. 8; c. 18; d. 5 **43.** a. 94 p, 144 n; b. 29 p, 36 n; c. 24 p, 28 n; d. 2 p, 2 n; e. 27 p, 33 n; f. 24 p, 30 n **45.** a. $^{12}_6\text{B}$; b. $^{15}_7\text{N}$; c. $^{35}_{17}\text{Cl}$; d. $^{235}_{92}\text{U}$; e. $^{14}_6\text{C}$; f. $^{31}_{15}\text{P}$ **47.** $^{151}_{63}\text{Eu}^{3+}$; $^{118}_{50}\text{Sn}^{2+}$; $^{99}_{33}\text{As}^{3+}$, 30 e; $^{128}_{52}\text{Te}^{2-}$, 52 p, 76 n, 2-; $^{32}_{16}\text{S}$, 0; $^{204}_{81}\text{Ti}^{+}$, 80 e; $^{195}_{78}\text{Pt}$, 78 p, 117 n, 78 e, 0 **51.** Metals: Mg, Ti, Au, Bi, Ge, Eu, Am; Nonmetals: Si, B, At, Rn, Br **53.** a, d **55.** Metallic character increases down a group. **57.** a. lose, Na^{+} ; b. lose, Sr^{2+} ; c. lose, Ba^{2+} ; d. gain, I^{-} ; e. lose, Al^{3+} ; f. gain, S^{2-} **59.** a. sodium chloride; b. rubidium oxide; c. calcium sulfide; d. aluminum iodide **61.** a. chromium(VI) oxide; b. chromium(III) oxide; c. aluminum oxide; d. sodium hydride; e. calcium bromide; f. zinc chloride **63.** a. potassium perchlorate; b. calcium phosphate; c. aluminum sulfate; d. lead(II) nitrate **65.** a. nitrogen triiodide; b. sulfur difluoride; c. phosphorus trichloride; d. dinitrogen tetrafluoride **67.** a. copper(I) iodide; b. copper(II) iodide; c. cobalt(II) iodide; d. sodium carbonate; e. sodium hydrogen carbonate or sodium bicarbonate; f. tetrasulfur tetranitride; g. sulfur hexafluoride; h. sodium hypochlorite; i. barium chromate; j. ammonium nitrate **69.** a. CsBr; b. BaSO_4 ; c. NH_4Cl ; d. ClO ; e. SiCl_4 ; f. ClF_3 ; g. BeO ; h. MgF_2 **71.** a. Na_2O ; b. Na_2O_2 ; c. KCN ; d. $\text{Cu}(\text{NO}_3)_2$; e. SeBr_4 ; f. PbS ; g. PbS_2 ; h. CuCl ; i. GaAs (from the positions in the periodic table, Ga^{3+} and As^{3-} are the predicted ions); j. CdSe ; k. ZnS ; l. HNO_3 ; m. P_2O_5 **73.** Yes, 1.0 g H would react with 37.0 g ^{37}Cl and 1.0 g H would react with 35.0 g ^{35}Cl . No, the mass ratio of H/Cl would always be 1 g H/37 g Cl for ^{37}Cl and 1 g H/35 g Cl for ^{35}Cl . As long as we had pure ^{35}Cl or pure ^{37}Cl , these ratios will always hold. If we have a mixture (such as the natural abundance of chlorine), the ratio will also be constant as long as the composition of the mixture of the two isotopes does not change. **75.** a. nitric acid; b. perchloric acid; c. acetic acid; d. sulfuric acid; e. phosphoric acid **77.** a. lead(II) acetate; b. copper(II) sulfate; c. calcium oxide; d. magnesium sulfate; e. magnesium hydroxide; f. calcium sulfate; g. dinitrogen monoxide or nitrous oxide (common) **79.** All contain 12 hydrogen atoms. **81.** a. Ca_3N_2 ; calcium nitride; b. K_2O ; potassium oxide; c. RbF ; rubidium fluoride; d. MgS ; magnesium sulfide; e. BaI_2 ; barium iodide; f. Al_2Se_3 ; aluminum selenide; g. Cs_3P ; cesium phosphide; h. InBr_3 ; indium(III) bromide (In forms compounds with +1 and +3 ions. You would predict a +3 ion from the position of In in the periodic table.) **83.** Cu, Ag, and Au **85.** The ratio of the masses of R that combine with 1.00 g Q is 3:1, as expected by the law of multiple proportions. R_3Q is the formula of the first compound. **87.** a. The compounds are isomers of each other. Isomers are compounds with the same formula but the atoms are attached differently, resulting in different properties. b. When wood burns, most of the solid material is converted to gases, which escape. c. Atoms are not an indivisible particle. Atoms are composed of electrons, neutrons, and protons. d. The two hydride samples contain different isotopes of either hydrogen and/or lithium. Isotopes may have different masses but have similar chemical properties.

Chapter 3

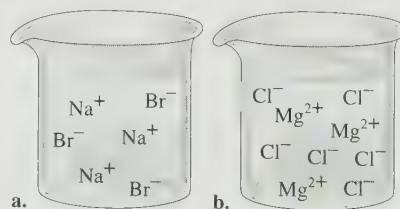
19. The molecular formula gives the actual number of atoms of each element in a molecule (or formula unit) of a compound. The empirical formula gives the simplest whole-number ratio of atoms of each element in a molecule. The molecular formula is a whole number multiple of the empirical formula. If that multiplier is one, the molecular and empirical formulas are the same. **21.** 24.31 amu **23.** 48% ^{151}Eu and 52% ^{153}Eu **25.** There are three peaks in the mass spectrum, each 2 mass units apart. This is consistent with two isotopes, differing in mass by two mass units. **27.** 4.64×10^{-20} g Fe **29.** 1.00×10^{22} atoms C **31.** Al_2O_3 , 101.96 g/mol; Na_3AlF_6 , 209.95 g/mol **33.** a. 17.03 g/mol; b. 32.05 g/mol; c. 252.08 g/mol **35.** a. 0.0587 mol NH_3 ; b. 0.0312 mol N_2H_4 ; c. 3.97×10^{-3} mol $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ **37.** a. 85.2 g NH_3 ; b. 160. g N_2H_4 ; c. 1260 g $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ **39.** a. 70.1 g N; b. 140. g N; c. 140. g N **41.** a. 3.54×10^{22} molecules NH_3 ; b. 1.88×10^{22} molecules N_2H_4 ;

c. 2.39×10^{21} formula units $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ **43.** a. 3.54×10^{22} atoms N; b. 3.76×10^{22} atoms N; c. 4.78×10^{21} atoms N **45.** 176.12 g/mol; 2.839×10^{-3} mol; 1.710×10^{21} molecules **47.** a. 4.13×10^{-4} mol; b. 9.40×10^{-2} mol; c. 1.661×10^{-22} mol; d. 6.592×10^{-5} mol **49.** a. 5.59×10^{-2} g; b. 4.00 g; c. 0.433 g; d. 4.653×10^{-23} g; e. 1.00×10^4 g **51.** a. 294.30 g/mol; b. 3.40×10^{-2} mol; c. 459 g; d. 1.0×10^{19} molecules; e. 4.9×10^{21} atoms; f. 4.9×10^{-13} g; g. 4.887×10^{-22} g **53.** 13.35% Y, 41.22% Ba, 28.62% Cu, 16.81% O **55.** $\text{NO}_2 = \text{N}_2\text{O}_4 < \text{NO} < \text{N}_2\text{O}$ **57.** 1360 g/mol **59.** a. 39.99% C, 6.713% H, 53.30% O; b. 40.00% C, 6.714% H, 53.29% O; c. 40.00% C, 6.714% H, 53.29% O (all the same except for rounding differences) **61.** a. NO_2 ; b. CH_2 ; c. P_2O_5 ; d. CH_2O **63.** TiO_2 **65.** compound I: HgO ; compound II: Hg_2O **67.** NO_2 , N_2O_4 **69.** $\text{C}_3\text{H}_5\text{O}_2$; $\text{C}_6\text{H}_{10}\text{O}_4$ **71.** C_3H_8 **73.** C_3H_4 , C_9H_{12} **75.** a. $4\text{Fe(s)} + 3\text{O}_2\text{(g)} \rightarrow 2\text{Fe}_2\text{O}_3\text{(s)}$; b. $\text{Ca(s)} + 2\text{H}_2\text{O(l)} \rightarrow \text{Ca(OH)}_2\text{(aq)} + \text{H}_2\text{(g)}$; c. $\text{Ba(OH)}_2\text{(aq)} + \text{H}_2\text{SO}_4\text{(aq)} \rightarrow \text{BaSO}_4\text{(s)} + 2\text{H}_2\text{O(l)}$ **77.** a. $\text{Cu(s)} + 2\text{AgNO}_3\text{(aq)} \rightarrow 2\text{Ag(s)} + \text{Cu(NO}_3)_2\text{(aq)}$; b. $\text{Zn(s)} + 2\text{HCl(aq)} \rightarrow \text{ZnCl}_2\text{(aq)} + \text{H}_2\text{(g)}$; c. $\text{Au}_2\text{S}_3\text{(s)} + 3\text{H}_2\text{(g)} \rightarrow 2\text{Au(s)} + 3\text{H}_2\text{S(g)}$ **79.** a. $2\text{C}_6\text{H}_6\text{(l)} + 15\text{O}_2\text{(g)} \rightarrow 12\text{CO}_2\text{(g)} + 6\text{H}_2\text{O(g)}$; b. $\text{C}_4\text{H}_{10}\text{(g)} + 13\text{O}_2\text{(g)} \rightarrow 8\text{CO}_2\text{(g)} + 10\text{H}_2\text{O(g)}$; c. $\text{C}_{12}\text{H}_{22}\text{O}_{11}\text{(s)} + 12\text{O}_2\text{(g)} \rightarrow 12\text{CO}_2\text{(g)} + 11\text{H}_2\text{O(g)}$; d. $4\text{Fe(s)} + 3\text{O}_2\text{(g)} \rightarrow 2\text{Fe}_2\text{O}_3\text{(s)}$; e. $4\text{FeO(s)} + \text{O}_2\text{(g)} \rightarrow 2\text{Fe}_2\text{O}_3\text{(s)}$ **81.** a. $\text{SiO}_2\text{(s)} + 2\text{C(s)} \rightarrow \text{Si(s)} + 2\text{CO(g)}$; b. $\text{SiCl}_4\text{(l)} + 2\text{Mg(s)} \rightarrow \text{Si(s)} + 2\text{MgCl}_2\text{(s)}$; c. $\text{Na}_2\text{SiF}_6\text{(s)} + 4\text{Na(s)} \rightarrow \text{Si(s)} + 6\text{NaF(s)}$ **83.** $\text{C}_{12}\text{H}_{22}\text{O}_{11}\text{(aq)} + \text{H}_2\text{O(l)} \rightarrow 4\text{C}_2\text{H}_5\text{OH(aq)} + 4\text{CO}_2\text{(g)}$ **85.** 6.51 g Cr_2O_3 , 1.20 g N_2 , 3.09 g H_2O **87.** 4.355 kg **89.** 7.2×10^4 g coke **91.** a. 65.01% Pt; 9.337% N; 2.015% H; 23.63% Cl; b. 72.3 g $\text{Pt(NH}_3)_2\text{Cl}_2$; 35.9 g KCl **93.** a. stoichiometric mixture; b. I_2 ; c. Mg; d. Mg; e. stoichiometric mixture; f. I_2 ; g. stoichiometric mixture; h. I_2 ; i. Mg **95.** a. 18.0 g HgBr_2 ; 1.03 g Br_2 excess; b. 35.0 g HgBr_2 **97.** 1300 g CaSO_4 , 630 g H_3PO_4 **99.** 82.8% **101.** 1.20×10^3 kg = 1.20 metric tons **103.** Mn, 54.94 amu **105.** 9.25×10^{22} H atoms **107.** 4.30×10^{-2} mol; 2.50 g **109.** 5 **111.** 42.8% **113.** 86.2% **115.** $\text{C}_{20}\text{H}_{30}\text{O}$ **117.** $\text{C}_7\text{H}_5\text{N}_3\text{O}_6$ **119.** 1.8×10^6 g $\text{Cu(NH}_3)_4\text{Cl}_2$; 5.9×10^5 g NH_3 **121.** 207 amu, Pb **123.** Al_2Se_3 **125.** 0.48 mol

Chapter 4

9. Solubility refers to how much dissolves. Electrolyte refers to whether or not ions are produced.

11.



c. For answers c–i, we will describe what should be in each solution. For c, the drawing should have three times as many NO_3^{-} anions as Al^{3+} cations. d. The drawing should have twice as many NH_4^{+} cations as SO_4^{2-} anions. e. The drawing should have equal numbers of Na^{+} cations and OH^{-} anions. f. The drawing should have equal numbers of Fe^{2+} cations and SO_4^{2-} anions. g. The drawing should have equal numbers of K^{+} cations and MnO_4^{-} anions. h. The drawing should have equal numbers of H^{+} cations and ClO_4^{-} anions. i. The drawing should have equal numbers of NH_4^{+} cations and $\text{C}_2\text{H}_3\text{O}_2^{-}$ anions. **13.** $\text{CaCl}_2\text{(s)} \rightarrow \text{Ca}^{2+}\text{(aq)} + 2\text{Cl}^{-}\text{(aq)}$ **15.** a. 0.2677 M; b. 1.255×10^{-3} M; c. 8.065×10^{-3} M **17.** a. $M_{\text{Ca}^{2+}} = 0.15$ M, $M_{\text{Cl}^{-}} = 0.30$ M; b. $M_{\text{Al}^{3+}} = 0.26$ M, $M_{\text{NO}_3^{-}} = 0.78$ M; c. $M_{\text{K}^{+}} = 0.50$ M, $M_{\text{Cr}_2\text{O}_7^{2-}} = 0.25$ M; d. $M_{\text{Al}^{3+}} = 4.0 \times 10^{-3}$ M, $M_{\text{SO}_4^{2-}} = 6.0 \times 10^{-3}$ M **19.** 100.0 mL of 0.30 M AlCl_3 **21.** 41.7 mL **23.** a. Place 20.0 g NaOH in a 2-L volumetric flask; add water to dissolve the NaOH and fill to the mark. b. Add 500. mL of the 1.00 M NaOH stock solution to a 2-L volumetric flask; fill to the mark with water. c. As in a, instead using 38.8 g K_2CrO_4 . d. As in b, instead using 114 mL of 1.75 M K_2CrO_4 stock

solution. **25.** $M_{\text{NH}_4^+} = 0.272 \text{ M}$, $M_{\text{SO}_4^{2-}} = 0.136 \text{ M}$ **27.** $5.94 \times 10^{-8} \text{ M}$ steroid **29.** $\text{BaSO}_4(\text{s})$; **b.** $\text{PbCl}_2(\text{s})$; **c.** $\text{Ag}_3\text{PO}_4(\text{s})$; **d.** $\text{Fe}(\text{OH})_3(\text{s})$ **31. a.** $\text{BaCl}_2(\text{aq}) + \text{Na}_2\text{SO}_4(\text{aq}) \rightarrow \text{BaSO}_4(\text{s}) + 2\text{NaCl}(\text{aq})$; $\text{Ba}^{2+}(\text{aq}) + 2\text{Cl}^-(\text{aq}) + 2\text{Na}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{BaSO}_4(\text{s}) + 2\text{Na}^+(\text{aq}) + 2\text{Cl}^-(\text{aq})$; $\text{Ba}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{BaSO}_4(\text{s})$; **b.** $\text{Pb}(\text{NO}_3)_2(\text{aq}) + 2\text{KCl}(\text{aq}) \rightarrow \text{PbCl}_2(\text{s}) + 2\text{KNO}_3(\text{aq})$; $\text{Pb}^{2+}(\text{aq}) + 2\text{NO}_3^-(\text{aq}) + 2\text{K}^+(\text{aq}) + 2\text{Cl}^-(\text{aq}) \rightarrow \text{PbCl}_2(\text{s}) + 2\text{K}^+(\text{aq}) + 2\text{NO}_3^-(\text{aq})$; $\text{Pb}^{2+}(\text{aq}) + 2\text{Cl}^-(\text{aq}) \rightarrow \text{PbCl}_2(\text{s})$; **c.** $3\text{AgNO}_3(\text{aq}) + \text{Na}_3\text{PO}_4(\text{aq}) \rightarrow \text{Ag}_3\text{PO}_4(\text{s}) + 3\text{NaNO}_3(\text{aq})$; $3\text{Ag}^+(\text{aq}) + 3\text{NO}_3^-(\text{aq}) + 3\text{Na}^+(\text{aq}) + \text{PO}_4^{3-}(\text{aq}) \rightarrow \text{Ag}_3\text{PO}_4(\text{s}) + 3\text{Na}^+(\text{aq}) + 3\text{NO}_3^-(\text{aq})$; $3\text{Ag}^+(\text{aq}) + \text{PO}_4^{3-}(\text{aq}) \rightarrow \text{Ag}_3\text{PO}_4(\text{s})$; **d.** $3\text{NaOH}(\text{aq}) + \text{Fe}(\text{NO}_3)_3(\text{aq}) \rightarrow \text{Fe}(\text{OH})_3(\text{s}) + 3\text{NaNO}_3(\text{aq})$; $3\text{Na}^+(\text{aq}) + 3\text{OH}^-(\text{aq}) + \text{Fe}^{3+}(\text{aq}) + 3\text{NO}_3^-(\text{aq}) \rightarrow \text{Fe}(\text{OH})_3(\text{s}) + 3\text{Na}^+(\text{aq}) + 3\text{NO}_3^-(\text{aq})$; $\text{Fe}^{3+}(\text{aq}) + 3\text{OH}^-(\text{aq}) \rightarrow \text{Fe}(\text{OH})_3(\text{s})$ **33. a.** $\text{CuSO}_4(\text{aq}) + \text{Na}_2\text{S}(\text{aq}) \rightarrow \text{CuS}(\text{s}) + \text{Na}_2\text{SO}_4(\text{aq})$; $\text{Cu}^{2+}(\text{aq}) + \text{S}^{2-}(\text{aq}) \rightarrow \text{CuS}(\text{s})$; the grey spheres are the Na^+ spectator ions and the blue-green spheres are the SO_4^{2-} spectator ions; **b.** $\text{CoCl}_2(\text{aq}) + 2\text{NaOH}(\text{aq}) \rightarrow \text{Co}(\text{OH})_2(\text{s}) + 2\text{NaCl}(\text{aq})$; $\text{Co}^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq}) \rightarrow \text{Co}(\text{OH})_2(\text{s})$; the grey spheres are the Na^+ spectator ions and the green spheres are the Cl^- spectator ions; **c.** $\text{AgNO}_3(\text{aq}) + \text{KI}(\text{aq}) \rightarrow \text{AgI}(\text{s}) + \text{KNO}_3(\text{aq})$; $\text{Ag}^+(\text{aq}) + \text{I}^-(\text{aq}) \rightarrow \text{AgI}(\text{s})$; the red spheres are the K^+ spectator ions and the blue spheres are the NO_3^- spectator ions **35. a.** $\text{Ba}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{BaSO}_4(\text{s})$; **b.** $\text{Pb}^{2+}(\text{aq}) + 2\text{Cl}^-(\text{aq}) \rightarrow \text{PbCl}_2(\text{s})$; **c.** No reaction; **d.** No reaction; **e.** $\text{Cu}^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq}) \rightarrow \text{Cu}(\text{OH})_2(\text{s})$ **37.** Three possibilities are: addition of K_2SO_4 solution to give a white ppt. of PbSO_4 ; addition of NaCl to give a white ppt. of PbCl_2 ; addition of K_2CrO_4 solution to give a bright yellow ppt. of PbCrO_4 **39.** 0.607 g **41.** 0.520 g $\text{Al}(\text{OH})_3$ **43.** 2.9 g AgCl ; 0 M Ag^+ ; 0.10 M NO_3^- ; 0.075 M Ca^{2+} ; 0.050 M Cl^- **45. a.** $2\text{HClO}_4(\text{aq}) + \text{Mg}(\text{OH})_2(\text{s}) \rightarrow \text{Mg}(\text{ClO}_4)_2(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$; $2\text{H}^+(\text{aq}) + 2\text{ClO}_4^-(\text{aq}) + \text{Mg}(\text{OH})_2(\text{s}) \rightarrow \text{Mg}^{2+}(\text{aq}) + 2\text{ClO}_4^-(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$; $2\text{H}^+(\text{aq}) + \text{Mg}(\text{OH})_2(\text{s}) \rightarrow \text{Mg}^{2+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$; **b.** $\text{HCN}(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow \text{NaCN}(\text{aq}) + \text{H}_2\text{O}(\text{l})$; $\text{HCN}(\text{aq}) + \text{Na}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{Na}^+(\text{aq}) + \text{CN}^-(\text{aq}) + \text{H}_2\text{O}(\text{l})$; $\text{HCN}(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l}) + \text{CN}^-(\text{aq})$; **c.** $\text{HCl}(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow \text{NaCl}(\text{aq}) + \text{H}_2\text{O}(\text{l})$; $\text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq}) + \text{Na}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq}) + \text{H}_2\text{O}(\text{l})$; $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l})$ **47. a.** $\text{KOH}(\text{aq}) + \text{HNO}_3(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l}) + \text{KNO}_3(\text{aq})$; $\text{K}^+(\text{aq}) + \text{OH}^-(\text{aq}) + \text{H}^+(\text{aq}) + \text{NO}_3^-(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l}) + \text{K}^+(\text{aq}) + \text{NO}_3^-(\text{aq})$; $\text{OH}^-(\text{aq}) + \text{H}^+(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l})$; **b.** $\text{Ba}(\text{OH})_2(\text{aq}) + 2\text{HCl}(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{BaCl}_2(\text{aq})$; $\text{Ba}^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq}) + 2\text{H}^+(\text{aq}) + 2\text{Cl}^-(\text{aq}) \rightarrow \text{Ba}^{2+}(\text{aq}) + 2\text{Cl}^-(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$; $\text{OH}^-(\text{aq}) + \text{H}^+(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l})$; **c.** $3\text{HClO}_4(\text{aq}) + \text{Fe}(\text{OH})_3(\text{s}) \rightarrow 3\text{H}_2\text{O}(\text{l}) + \text{Fe}(\text{ClO}_4)_3(\text{aq})$; $3\text{H}^+(\text{aq}) + 3\text{ClO}_4^-(\text{aq}) + \text{Fe}(\text{OH})_3(\text{s}) \rightarrow 3\text{H}_2\text{O}(\text{l}) + \text{Fe}^{3+}(\text{aq}) + 3\text{ClO}_4^-(\text{aq})$; $3\text{H}^+(\text{aq}) + \text{Fe}(\text{OH})_3(\text{s}) \rightarrow 3\text{H}_2\text{O}(\text{l}) + \text{Fe}^{3+}(\text{aq})$ **49. a.** 100. mL; **b.** 66.7 mL; **c.** 50.0 mL **51.** Basic, 0.250 M NO_3^- , 2.50 M Na^+ , 2.25 M OH^- **53.** 0.102 M **55.** 0.4178 g **57. a.** K, +1; O, -2; Mn, +7; **b.** Ni, +4; O, -2; **c.** Fe, +2; **d.** H, +1; O, -2; N, -3; P, +5; **e.** P, +3; O, -2; **f.** O, -2; Fe, +8; **g.** O, -2; F, -1; Xe, -6; **h.** S, +4; F, -1; **i.** C, +2; O, -2; **j.** Na, +1; O, -2; C, +3 **59. a.** Br, -1; **b.** Br, +1; **c.** Br, 0; **d.** Br, +7; **e.** Br, +3

61. Redox?	Oxidizing Agent	Reducing Agent	Substance Oxidized	Substance Reduced
a. Yes	O_2	CH_4	$\text{CH}_4(\text{C})$	$\text{O}_2(\text{O})$
b. Yes	HCl	Zn	Zn	$\text{HCl}(\text{H})$
c. No	—	—	—	—
d. Yes	O_3	NO	$\text{NO}(\text{N})$	$\text{O}_3(\text{O})$
e. Yes	H_2O_2	H_2O_2	$\text{H}_2\text{O}_2(\text{O})$	$\text{H}_2\text{O}_2(\text{O})$
f. Yes	CuCl	CuCl	$\text{CuCl}(\text{Cu})$	$\text{CuCl}(\text{Cu})$

63. a. $\text{Zn} + 2\text{HCl} \rightarrow \text{Zn}^{2+} + \text{H}_2 + 2\text{Cl}^-$; **b.** $2\text{H}^+ + 3\text{I}^- + \text{ClO}^- \rightarrow \text{I}_3^- + \text{Cl}^- + \text{H}_2\text{O}$; **c.** $7\text{H}_2\text{O} + 4\text{H}^+ + 3\text{As}_2\text{O}_3 + 4\text{NO}_3^- \rightarrow 4\text{NO} + 6\text{H}_3\text{AsO}_4$; **d.** $16\text{H}^+ + 2\text{MnO}_4^- + 10\text{Br}^- \rightarrow 5\text{Br}_2 + 2\text{Mn}^{2+} + 8\text{H}_2\text{O}$; **e.** $8\text{H}^+ + 3\text{CH}_3\text{OH} + \text{Cr}_2\text{O}_7^{2-} \rightarrow 2\text{Cr}^{3+} + 3\text{CH}_2\text{O} + 7\text{H}_2\text{O}$ **65. a.** $2\text{H}_2\text{O} + \text{Al} + \text{MnO}_4^- \rightarrow \text{Al}(\text{OH})_4^- + \text{MnO}_2$; **b.** $2\text{OH}^- + \text{Cl}_2 \rightarrow \text{Cl}^- + \text{ClO}^- + \text{H}_2\text{O}$; **c.** $\text{OH}^- + \text{H}_2\text{O} + \text{NO}_2^- + 2\text{Al} \rightarrow \text{NH}_3 + 2\text{AlO}_2^-$ **67.** $4\text{NaCl} +$

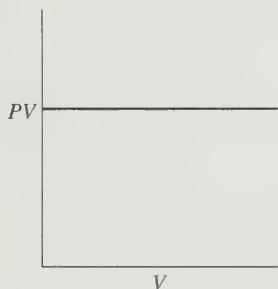
$2\text{H}_2\text{SO}_4 + \text{MnO}_2 \rightarrow 2\text{Na}_2\text{SO}_4 + \text{MnCl}_2 + \text{Cl}_2 + 2\text{H}_2\text{O}$ **69.** 0.0111 M **71. a.** AgNO_3 , $\text{Pb}(\text{NO}_3)_2$, and $\text{Hg}_2(\text{NO}_3)_2$ would form precipitates with the Cl^- ion; $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{AgCl}(\text{s})$; $\text{Pb}^{2+}(\text{aq}) + 2\text{Cl}^-(\text{aq}) \rightarrow \text{PbCl}_2(\text{s})$; $\text{Hg}_2^{2+}(\text{aq}) + 2\text{Cl}^-(\text{aq}) \rightarrow \text{Hg}_2\text{Cl}_2(\text{s})$; **b.** Na_2SO_4 , Na_2CO_3 , and Na_3PO_4 would form precipitates with the Ca^{2+} ion; $\text{Ca}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{CaSO}_4(\text{s})$; $\text{Ca}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) \rightarrow \text{CaCO}_3(\text{s})$; $3\text{Ca}^{2+}(\text{aq}) + 2\text{PO}_4^{3-}(\text{aq}) \rightarrow \text{Ca}_3(\text{PO}_4)_2(\text{s})$; **c.** NaOH , Na_2S , and Na_2CO_3 would form precipitates with the Fe^{3+} ion; $\text{Fe}^{3+}(\text{aq}) + 3\text{OH}^-(\text{aq}) \rightarrow \text{Fe}(\text{OH})_3(\text{s})$; $2\text{Fe}^{3+}(\text{aq}) + 3\text{S}^{2-}(\text{aq}) \rightarrow \text{Fe}_2\text{S}_3(\text{s})$; $2\text{Fe}^{3+}(\text{aq}) + 3\text{CO}_3^{2-}(\text{aq}) \rightarrow \text{Fe}_2(\text{CO}_3)_3(\text{s})$; **d.** BaCl_2 , $\text{Pb}(\text{NO}_3)_2$, and $\text{Ca}(\text{NO}_3)_2$ would form precipitates with the SO_4^{2-} ion; $\text{Ba}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{BaSO}_4(\text{s})$; $\text{Pb}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{PbSO}_4(\text{s})$; $\text{Ca}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{CaSO}_4(\text{s})$; **e.** Na_2SO_4 , NaCl , and NaI would form precipitates with the Hg_2^{2+} ion; $\text{Hg}_2^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{Hg}_2\text{SO}_4(\text{s})$; $\text{Hg}_2^{2+}(\text{aq}) + 2\text{Cl}^-(\text{aq}) \rightarrow \text{Hg}_2\text{Cl}_2(\text{s})$; $\text{Hg}_2^{2+}(\text{aq}) + 2\text{I}^-(\text{aq}) \rightarrow \text{Hg}_2\text{I}_2(\text{s})$; **f.** NaBr , Na_2CrO_4 , and Na_3PO_4 would form precipitates with the Ag^+ ion; $\text{Ag}^+(\text{aq}) + \text{Br}^-(\text{aq}) \rightarrow \text{AgBr}(\text{s})$; $2\text{Ag}^+(\text{aq}) + \text{CrO}_4^{2-}(\text{aq}) \rightarrow \text{Ag}_2\text{CrO}_4(\text{s})$; $3\text{Ag}^+(\text{aq}) + \text{PO}_4^{3-}(\text{aq}) \rightarrow \text{Ag}_3\text{PO}_4(\text{s})$ **73.** 18.8 g **75.** 39.49 mg/tablet; 67.00% **77.** 2.00 M **79. a.** 0.8393 M ; **b.** 5.010% **81.** $\text{C}_6\text{H}_5\text{O}_6$ **83.** $2\text{H}^+(\text{aq}) + \text{Mn}(\text{s}) + 2\text{HNO}_3(\text{aq}) \rightarrow \text{Mn}^{2+}(\text{aq}) + 2\text{NO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$; $3\text{H}_2\text{O}(\text{l}) + 2\text{Mn}^{2+}(\text{aq}) + 5\text{IO}_4^-(\text{aq}) \rightarrow 2\text{MnO}_4^-(\text{aq}) + 5\text{IO}_3^-(\text{aq}) + 6\text{H}^+(\text{aq})$ **85. a.** 24.8% Co, 29.7% Cl, 5.09% H, 40.4% O; **b.** $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$; **c.** $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}(\text{aq}) + 2\text{AgNO}_3(\text{aq}) \rightarrow 2\text{AgCl}(\text{s}) + \text{Co}(\text{NO}_3)_2(\text{aq}) + 6\text{H}_2\text{O}(\text{l})$; $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}(\text{aq}) + 2\text{NaOH}(\text{aq}) \rightarrow \text{Co}(\text{OH})_2(\text{s}) + 2\text{NaCl}(\text{aq}) + 6\text{H}_2\text{O}(\text{l})$; $4\text{Co}(\text{OH})_2(\text{s}) + \text{O}_2(\text{g}) \rightarrow 2\text{Co}_2\text{O}_3(\text{s}) + 4\text{H}_2\text{O}(\text{l})$ **87. a.** 7.000 M K^+ ; **b.** 0.750 M CrO_4^{2-} **89.** 0.123 g SO_4^{2-} , 60.0% SO_4^{2-} ; 61% K_2SO_4 and 39% Na_2SO_4 **91.** 57.6 mL **93. a.** $\text{MgO}(\text{s}) + 2\text{HCl}(\text{aq}) \rightarrow \text{MgCl}_2(\text{aq}) + \text{H}_2\text{O}(\text{l})$; $\text{Mg}(\text{OH})_2(\text{s}) + 2\text{HCl}(\text{aq}) \rightarrow \text{MgCl}_2(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$; $\text{Al}(\text{OH})_3(\text{s}) + 3\text{HCl}(\text{aq}) \rightarrow \text{AlCl}_3(\text{aq}) + 3\text{H}_2\text{O}(\text{l})$; **b.** MgO **95.** Citric acid has three acidic hydrogens per citric acid molecule. **97.** $0.07849 \pm 0.00016 \text{ M}$ or $0.0785 \pm 0.0002 \text{ M}$

Chapter 5

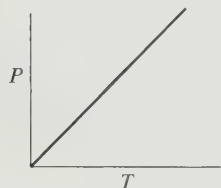
17. At constant n and T , $nRT = \text{constant}$, so $PV = k$ (Boyle's law). At constant P and n , $V = nRT/P = kT$ (Charles's law). **19.** The kinetic molecular theory assumes that gases do not exert forces on each other and that gas molecules are volumeless. Real gases do exert attractive forces on each other and real gases do have a volume. A gas behaves most ideally at low pressures and high temperatures. The effect of attractive forces is minimized at high temperatures since the gas molecules are moving very rapidly. At low pressure, the container volume is relatively large (P and V are inversely related) so the volume of the container that is taken up by the gas molecules is negligible. **21.** Graham's law of effusion can be used. Determine the relative effusion rate of the unknown gas to some known gas; then use Graham's law to determine the molar mass of the unknown. The ideal gas law also can be used to determine the molar mass. The appropriate form to use is molar mass = dRT/P . If the density, temperature, and pressure of the gas are known, then the molar mass can be calculated. **23.** Rigid container: pressure decreases (is halved) and the density is constant; flexible container: pressure is constant and the density increases (is doubled) **25. a.** $3.6 \times 10^3 \text{ mm Hg}$; **b.** $3.6 \times 10^3 \text{ torr}$; **c.** $4.9 \times 10^5 \text{ Pa}$; **d.** 71 psi **27.** 65 torr, $8.7 \times 10^3 \text{ Pa}$, $8.6 \times 10^{-2} \text{ atm}$ **29. a.** 642 torr, 0.845 atm; $8.56 \times 10^4 \text{ Pa}$; **b.** 975 torr; 1.28 atm; $1.30 \times 10^5 \text{ Pa}$; **c.** 517 torr; 850. torr **31.** 0.972 atm **33.** 44.8 L **35. a.** 14.0 L; **b.** $4.72 \times 10^{-2} \text{ mol}$; **c.** 678 K; **d.** 133 atm **37.** $4.44 \times 10^3 \text{ g He}$; $2.24 \times 10^3 \text{ g H}_2$ **39. a.** 69.6 K; **b.** 32.3 atm **41.** The balloon will burst **43.** 33.5 MPa **45.** $5.1 \times 10^4 \text{ torr}$ **47.** The volume of the balloon increases from 1.00 L to 2.82 L, so the change in volume is 1.82 L. **49.** 0.27 g **51.** 4.23 L O_2 ; 4.23 L CO_2 ; 4.23 L H_2O **53.** $1.5 \times 10^7 \text{ g Fe}$, $2.6 \times 10^7 \text{ g } 98\% \text{ H}_2\text{SO}_4$ **55.** 2.47 mol H_2O **57. a.** $2\text{CH}_4(\text{g}) + 2\text{NH}_3(\text{g}) + 3\text{O}_2(\text{g}) \rightarrow 2\text{HCN}(\text{g}) + 6\text{H}_2\text{O}(\text{g})$; **b.** 13.3 L **59.** 42.1 g/mol, C_3H_6 **61.** 5.77 g/L (SiCl_4), 4.60 g/L (SiHCl_3) **63.** 1.1 atm, $P_{\text{CO}_2} = 1.1 \text{ atm}$, $P_{\text{TOTAL}} = 2.1 \text{ atm}$ **65.** $P_{\text{H}_2} = 317 \text{ torr}$, $P_{\text{N}_2} = 50.7 \text{ torr}$, $P_{\text{TOTAL}} = 368 \text{ torr}$ **67. a.** $\chi_{\text{CH}_4} = 0.412$, $\chi_{\text{O}_2} = 0.588$; **b.** 0.161 mol; **c.** 1.06 g CH_4 , 3.03 g O_2 **69.** 0.990 atm; 0.625 g

71. 18.0% 73. 3.40×10^3 J/mol (273 K); 6.81×10^3 J/mol (546 K)
 75. CH_4 : 652 m/s (273 K); 921 m/s (546 K); N_2 : 493 m/s (273 K); 697 m/s (546 K) 77. Both the average kinetic energy and the average velocity will increase with an increase in temperature. 79. a. All the same; b. Flask C 81. NO 83. The relative rates of effusion of $^{12}\text{C}^{16}\text{O}$, $^{12}\text{C}^{17}\text{O}$, and $^{12}\text{C}^{18}\text{O}$ are 1.04, 1.02, and 1.00. Advantage: CO_2 isn't as toxic as CO. Disadvantages: Can get a mixture of oxygen isotopes in CO_2 , so some species would effuse at about the same rate. 85. a. 12.24 atm; b. 12.13 atm; c. The ideal gas law is high by 0.91%. 87. 5×10^{-7} atm, 1×10^{13} molecules/cm³ 89. 0.4 mL 91. $2\text{NO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{HNO}_3(\text{aq}) + \text{HNO}_2(\text{aq})$; $\text{SO}_3(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{SO}_4(\text{aq})$

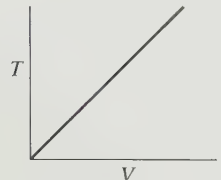
93. a.



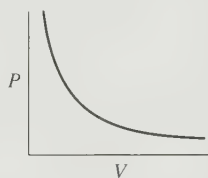
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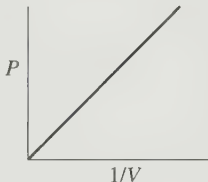
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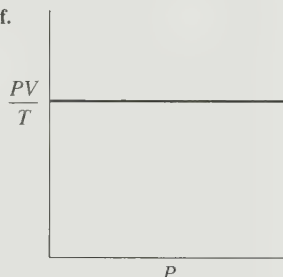
d.



e.



f.



95. MnCl_4 97. 1490 99. 24 torr 101. 4.1×10^6 L air; 7.42×10^5 L H_2
 103. 490 atm 105. $\text{Be}(\text{C}_5\text{H}_7\text{O}_2)_2$ has a molar mass of 207 g/mol and $\text{Be}(\text{C}_5\text{H}_7\text{O}_2)_2$ had a molar mass of 311 g/mol. The molar mass calculated from the first data set is 209 g/mol and from the second data set is 202 g/mol. These experiment results are close to the expected value of 207 g/mol for $\text{Be}(\text{C}_5\text{H}_7\text{O}_2)_2$. Thus we conclude from these data that beryllium is a divalent element with an atomic mass of 9.0 amu. 107. 13.3% N 109. The pressure will increase initially because H_2 will effuse into container A faster than air will escape. However, the pressures will equalize once the gases have had time to mix thoroughly. 111. CO_2 113. 13.4% CaO , 86.6% BaO 115. a. 8.7×10^3 L air/min; b. $\chi_{\text{CO}} = 0.0017$, $\chi_{\text{CO}_2} = 0.032$, $\chi_{\text{O}_2} = 0.13$, $\chi_{\text{N}_2} = 0.77$, $\chi_{\text{H}_2\text{O}} = 0.067$ 117. a. 1.01×10^4 g; b. 6.65×10^4 g; c. 8.7×10^3 g 119. a. 0.19 torr; b. 6.6×10^{15} molecules CO/cm^3

Chapter 6

9. A coffee-cup calorimeter is at constant pressure. The heat at constant P equals ΔH . A bomb calorimeter is at constant volume. The heat at constant V equals ΔE . 11. Al. Al has a higher heat capacity and a lower density than Fe. The same amount of heat could be dissipated by a smaller mass of Al. 13. A function whose change depends only on the initial and final states and not on the pathway from the initial to the final state. If H

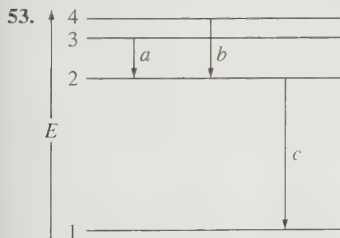
and E were not state functions, the law of conservation of energy (first law) would not be true. 15. Standard enthalpies of formation provide a reference point, allowing ΔH comparisons. 17. 150 J 19. 1.0 kg object with velocity of 2.0 m/s. 21. a. 36 kJ; b. 35 kJ; c. -85 kJ; d. all 23. -21 kJ 25. 10. L · atm = 1.0×10^3 J 27. $q = 30.9$ kJ, $w = -12.4$ kJ, $\Delta E = 18.5$ kJ 29. This is an endothermic reaction, so heat must be absorbed to convert reactants into products. The high-temperature environment of internal combustion engines provides the heat. 31. a. endothermic; b. exothermic; c. exothermic; d. endothermic 33. a. -1650 kJ; b. -826 kJ; c. -7.39 kJ; d. -34.4 kJ 35. 4400 g C_3H_8 37. $\text{H}_2\text{O}(\text{l})$; 2.30×10^3 J; $\text{Hg}(\text{l})$; 140°C 39. 0.129 J/g · °C, 26.7 J/mol · °C 41. 311 K 43. 0.25 J/g · °C 45. -66 kJ/mol 47. 39.2°C 49. 1.65 kJ/°C; -25.2 kJ/g; -3830 kJ/mol 51. -220.8 kJ 53. -58.0 kJ 55. -233 kJ 57. 28.4 kJ 59. The enthalpy change for the formation of one mole of a compound from its elements, with all substances in their standard states. $\text{Na}(\text{s}) + \frac{1}{2}\text{Cl}_2(\text{g}) \rightarrow \text{NaCl}(\text{s})$; $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$; $6\text{C}_{\text{graphite}}(\text{s}) + 6\text{H}_2(\text{g}) + 3\text{O}_2(\text{g}) \rightarrow \text{C}_6\text{H}_{12}\text{O}_6(\text{s})$; $\text{Pb}(\text{s}) + \text{S}(\text{s}) + 2\text{O}_2(\text{g}) \rightarrow \text{PbSO}_4(\text{s})$ 61. a. -940. kJ; b. -265 kJ; c. -176 kJ 63. a. -908 kJ, -112 kJ, -140. kJ; b. $12\text{NH}_3(\text{g}) + 21\text{O}_2(\text{g}) \rightarrow 8\text{HNO}_3(\text{aq}) + 4\text{NO}(\text{g}) + 14\text{H}_2\text{O}(\text{g})$, exothermic 65. -2677 kJ 67. -169 kJ/mol 69. -29.67 kJ/g 71. For $\text{C}_3\text{H}_8(\text{g})$, -50.37 kJ/g vs. -47.7 kJ/g for octane. Because of the low boiling point of propane, there are extra safety hazards associated with using the necessary high-pressure compressed gas tanks. 73. 1.05×10^5 L 75. a. $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SO}_3(\text{g})$; $w > 0$; b. $\text{COCl}_2(\text{g}) \rightarrow \text{CO}(\text{g}) + \text{Cl}_2(\text{g})$; $w < 0$; c. $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}(\text{g})$; $w = 0$; Compare the sum of the coefficients of all the product gases in the balanced equation to the sum of the coefficients of all the reactant gases. When a balanced reaction has more mol of product gases than mol of reactant gases, then the reaction will expand in volume (ΔV is positive) and the system does work on the surroundings ($w < 0$). When a balanced reaction has a decrease in the mol of gas from reactants to products, then the reaction will contract in volume (ΔV is negative) and the surroundings does compression work on the system ($w > 0$). When there is no change in the mol of gas from reactants to products, then $\Delta V = 0$ and $w = 0$. 77. 25 J 79. 75.0 g 81. -4.2 kJ 83. 25.91°C 85. a. 632 kJ; b. $\text{C}_2\text{H}_2(\text{g})$ 87. a. -361 kJ; b. -199 kJ; c. -227 kJ; d. -112 kJ 89. a. $\text{C}_{12}\text{H}_{22}\text{O}_{11}(\text{s}) + 12\text{O}_2(\text{g}) \rightarrow 12\text{CO}_2(\text{g}) + 11\text{H}_2\text{O}(\text{l})$; b. -5630 kJ; c. -5630 kJ 91. 37 m² 93. 1×10^4 steps

Chapter 7

15. Planck found it necessary to assume quantized energies to explain the radiation that heated bodies emit. Einstein's analysis of the photoelectric effect. 17. Only very small particles with a tiny mass exhibit wave and particle properties—for example, an electron. Some evidence supporting the wave properties of matter are (1) electrons can be diffracted like light and (2) the electron microscope uses electrons in a fashion similar to the way in which light is used in a light microscope. 19. n : gives the energy (it completely specifies the energy only for the H atom or ions with one electron) and the relative size of the orbitals; ℓ : gives the type (shape) of orbital; m_ℓ : gives information about the direction in which the orbital is pointing 21. A surface where the probability of finding an electron is zero. 23. No, the spin is a convenient model. Since we cannot locate or "see" the electron, we cannot see if it is spinning. 25. The outermost electrons are the valence electrons. When atoms interact, the outermost electrons are involved in these interactions. In addition, how tightly the nucleus holds these outermost electrons determines atomic size, ionization energy, and other properties of atoms. Elements in the same group have similar valence electron configurations and, as a result, similar chemical properties. 27. Across a period, the positive charge from the nucleus increases as protons are added. The number of electrons also increases, but these outer electrons do not completely shield the increasing nuclear charge from each other. The general result is that the outer electrons are more

strongly held by the nucleus as one goes across a period, which results in larger ionization energies (and smaller size). Aluminum is out of order because the electrons in the filled $3s$ orbital shield some of the nuclear charge from the $3p$ electron. Hence, the $3p$ electron is less tightly bound than a $3s$ electron, resulting in a lower ionization energy for aluminum as compared to magnesium. The ionization energy of sulfur is lower than that of phosphorus because of the extra electron–electron repulsions in the doubly occupied sulfur $3p$ orbital. These added repulsions, which are not present in phosphorus, makes it slightly easier to remove an electron from sulfur as compared to phosphorus. **29.** $P(g) \rightarrow P^+(g) + e^-$; $P(g) + e^- \rightarrow P^-(g)$

31. The valence electrons are strongly attracted to the nucleus for elements with large ionization energies. One would expect these species to readily accept another electron and have very exothermic electron affinities. The noble gases are an exception; they have a large ionization energy but an endothermic electron affinity. Noble gases have a stable arrangement of electrons. Adding an electron disrupts this stable arrangement, resulting in unfavorable electron affinities. **33.** For hydrogen, all orbitals with the same value of n have the same energy. For polyatomic atoms/ions, the energy of the orbitals also depends on ℓ . Since there are more nondegenerate energy levels for polyatomic atoms/ions as compared with hydrogen, then there are many more possible electronic transitions resulting in more complicated line spectra. **35.** Yes, the maximum number of unpaired electrons in any configuration corresponds to a minimum in electron–electron repulsions. **37.** Ionization energy applies to the removal of the electron from the atom in the gas phase. The work function applies to the removal of an electron from the solid. **39.** $3.84 \times 10^{14} \text{ s}^{-1}$
41. $3.0 \times 10^{10} \text{ s}^{-1}$, $2.0 \times 10^{-23} \text{ J/photon}$, 12 J/mol **43.** Wave a has the longer wavelength ($4.0 \times 10^{-4} \text{ m}$). Wave b has the higher frequency ($1.5 \times 10^{12} \text{ s}^{-1}$) and larger photon energy ($9.9 \times 10^{-22} \text{ J}$). Since both of these waves represent electromagnetic radiation, they should travel at the same speed, c , the speed of light. Both waves represent infrared radiation. **45.** 427.7 nm
47. a. $1.5 \times 10^{-6} \text{ nm}$; **b.** $4.4 \times 10^{-25} \text{ nm}$ **49.** 2.4 nm **51. a.** 656.7 nm (visible); **b.** 486.4 nm (visible); **c.** 121.6 nm (ultraviolet)



53. **4.** $n = 1 \rightarrow n = 5$, $\lambda = 95.00 \text{ nm}$; $n = 2 \rightarrow n = 6$, $\lambda = 410.4 \text{ nm}$; visible light has sufficient energy for the $n = 2 \rightarrow n = 6$ transition but does not have sufficient energy for the $n = 1 \rightarrow n = 5$ transition. **57.** $n = 6$
59. a. $5.79 \times 10^{-4} \text{ m}$; **b.** $3.64 \times 10^{-33} \text{ m}$; **c.** The diameter of an H atom is roughly $1.0 \times 10^{-8} \text{ cm}$. The uncertainty in position is much larger than the size of the atom. **d.** The uncertainty is insignificant compared to the size of a baseball. **61.** $n = 1, 2, 3, \dots$; $\ell = 0, 1, 2, \dots (n - 1)$; $m_\ell = -\ell, \dots, -2, -1, 0, 1, 2, \dots, +\ell$. **63. b.** ℓ must be $< n$; **d.** For $\ell = 0$, $m_\ell = 0$ only **65.** ψ^2 gives the probability of finding the electron at that point. **67.** 3; 1; 5; 25; 16 **69. a.** 32; **b.** 8; **c.** 25; **d.** 10; **e.** 6 **71.** Si: $1s^2 2s^2 2p^6 3s^2 3p^2$ or $[\text{Ne}] 3s^2 3p^2$; Ga: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^1$ or $[\text{Ar}] 4s^2 3d^{10} 4p^1$; As: $[\text{Ar}] 4s^2 3d^{10} 4p^3$; Ge: $[\text{Ar}] 4s^2 3d^{10} 4p^2$; Al: $[\text{Ne}] 3s^2 3p^1$; Cd: $[\text{Kr}] 5s^2 4d^{10}$; S: $[\text{Ne}] 3s^2 3p^4$; Se: $[\text{Ar}] 4s^2 3d^{10} 4p^4$ **73.** Sc: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$; Fe: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$; P: $1s^2 2s^2 2p^6 3s^2 3p^3$; Cs: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^1$ (Actual: $[\text{Xe}] 6s^2 4f^7$); Pt: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^8$ (Actual: $[\text{Xe}] 6s^1 4f^{14} 5d^9$); Xe: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6$; Br: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^5$; **75.** Cr, Cu, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Pt, Au **77. a.** I: $[\text{Kr}] 5s^2 4d^{10} 5p^5$; **b.** element 120: $[\text{Rn}] 7s^2 5f^{14} 6d^{10} 7p^8 8s^2$; **c.** Rn: $[\text{Xe}] 6s^2 4f^{14} 5d^{10} 6p^6$; **d.** Cr: $[\text{Ar}] 4s^1 3d^5$

79. B: $1s^2 2s^2 2p^1$

	n	ℓ	m_ℓ	m_s
1s	1	0	0	$+\frac{1}{2}$
1s	1	0	0	$-\frac{1}{2}$
2s	2	0	0	$+\frac{1}{2}$
2s	2	0	0	$-\frac{1}{2}$
2p	2	1	-1	$+\frac{1}{2}$

N: $1s^2 2s^2 2p^3$

	n	ℓ	m_ℓ	m_s
1s	1	0	0	$+\frac{1}{2}$
1s	1	0	0	$-\frac{1}{2}$
2s	2	0	0	$+\frac{1}{2}$
2s	2	0	0	$-\frac{1}{2}$
2p	2	1	-1	$+\frac{1}{2}$
2p	2	1	0	$+\frac{1}{2}$
2p	2	1	+1	$+\frac{1}{2}$

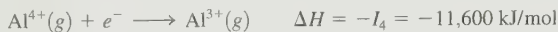
For boron, there are six possibilities for the $2p$ electron. For nitrogen, all the $2p$ electrons could have $m_s = -\frac{1}{2}$. **81.** none; an excited state; energy released **83.** Li (1 unpaired electron), N (3 unpaired electrons), Ni (2 unpaired electrons), and Te (2 unpaired electrons) are all expected to be paramagnetic because they have unpaired electrons. **85. a.** $\text{Be} < \text{Mg} < \text{Ca}$; **b.** $\text{Xe} < \text{I} < \text{Te}$; **c.** $\text{Ge} < \text{Ga} < \text{In}$ **87. a.** $\text{Ca} < \text{Mg} < \text{Be}$; **b.** $\text{Te} < \text{I} < \text{Xe}$; **c.** $\text{In} < \text{Ga} < \text{Ge}$ **89. a.** Li; **b.** P; **c.** O^+ ; **d.** Cl; **e.** Cu **91. a.** $[\text{Rn}] 7s^2 5f^{14} 6d^4$; **b.** W; **c.** Using Sg as a symbol for element 106, SgO_3 and SgO_4^{2-} probably would form (similar to Cr). **93.** Se is an exception to the general ionization trend. There are extra electron–electron repulsions in Se because two electrons are in the same $4p$ orbital, resulting in a lower ionization energy than expected. **95. a.** C, Br; **b.** N, Ar; **c.** C, Br **97. a.** $\text{Se} < \text{S}$; **b.** $\text{I} < \text{Br} < \text{F} < \text{Cl}$ **99.** Electron–electron repulsions are much greater in O than S^- because the electron goes into a smaller $2p$ orbital vs. the larger $3p$ orbital on sulfur, resulting in a more favorable (more exothermic) E.A. for sulfur. **101. a.** -1445 kJ/mol ; **b.** -580 kJ/mol **103.** potassium peroxide, K_2O_2 ; K^{2+} unstable **105.** $6.582 \times 10^{14} \text{ s}^{-1}$; $4.361 \times 10^{-19} \text{ J}$ **107.** Yes; the ionization energy general trend decreases down a group and the atomic radius trend increases down a group. The data in Table 7.8 confirm both of these general trends. **109. a.** $4\text{Li}(s) + \text{O}_2(g) \rightarrow 2\text{Li}_2\text{O}(s)$; **b.** $2\text{K}(s) + \text{S}(s) \rightarrow \text{K}_2\text{S}(s)$ **111.** 386 nm **113.** 200 s **115.** $\lambda = 4.104 \times 10^{-5} \text{ cm}$ so violet light is emitted. **117. a.** true for H only; **b.** true for all atoms; **c.** true for all atoms **119. a.** 20; **b.** 18; **c.** 10; **d.** 24 **121.** The element with the smallest first ionization energy (I_1) is Al (the green plot), the next highest I_1 belongs to Mg (the blue plot), and Si has the largest I_1 (the purple plot). Mg is the element with the huge jump between I_2 and I_3 ; it has two valence electrons so the third electron removed is an inner-core electron. Inner-core electrons are always much more difficult to remove as compared to valence electrons because they are closer to the nucleus, on average, as compared to the valence electrons. **123.** Valence electrons are easier to remove than inner-core electrons. The large difference in energy between I_2 and I_3 indicates that this element has two valence electrons. The element is most likely an alkaline earth metal because alkaline earth metals have two valence electrons. **125. a.** 146 kJ ; **b.** 407 kJ ; **c.** 1117 kJ ; **d.** 1524 kJ **127.** 4 **129.** For $r = a_0$ and $\theta = 0^\circ$, $\psi^2 = 2.46 \times 10^{28}$. For $r = a_0$ and $\theta = 90^\circ$, $\psi^2 = 0$. As expected, the xy plane is a node for the $2p_z$ atomic orbital.

131. a.

1							2
3							4
5	6	7	8	9	10	11	12
13	14	15	16	17	18	19	20

b. 2, 4, 12, and 20; **c.** There are many possibilities. One example of each formula is $\text{XY} = 1 + 11$, $\text{XY}_2 = 6 + 11$, $\text{X}_2\text{Y} = 1 + 10$, $\text{XY}_3 = 7 + 11$, and $\text{X}_2\text{Y}_3 = 7 + 10$; **d.** 6; **e.** 0; **f.** 18 **133. a.** As we remove succeeding electrons, the electron being removed is closer to the nucleus and there are fewer electrons left repelling it. The remaining electrons are more strongly attracted to the nucleus and it takes more energy to remove these electrons. **b.** For I_4 , we begin removing an electron with $n = 2$. For I_3 , we

removed an electron with $n = 3$. In going from $n = 3$ to $n = 2$ there is a big jump in ionization energy because the $n = 2$ electrons (inner core) are much closer to the nucleus on the average than the $n = 3$ electrons (valence electrons). Since the $n = 2$ electrons are closer to the nucleus, they are held more tightly and require a much larger amount of energy to remove them. **c.** Al^{4+} ; the electron affinity for Al^{4+} is ΔH for the reaction



d. The greater the number of electrons, the greater the size. So

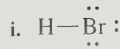
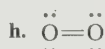
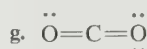
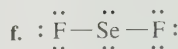
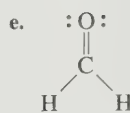
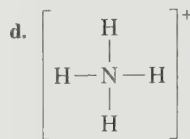
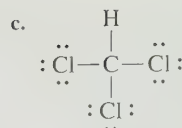
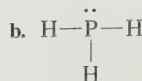
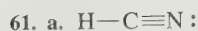


Chapter 8

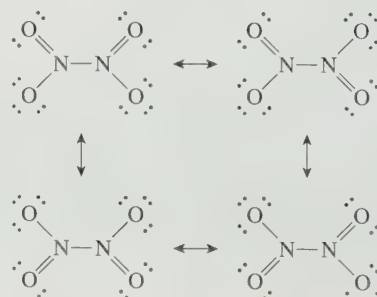
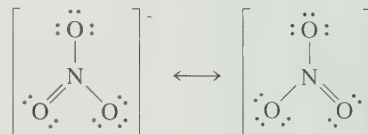
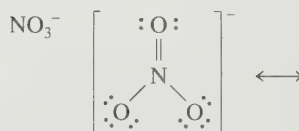
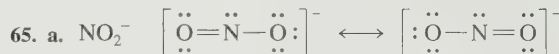
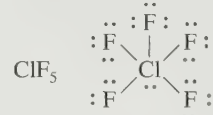
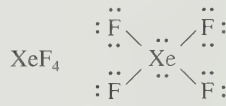
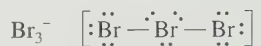
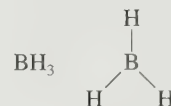
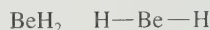
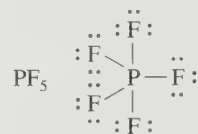
13. a. Electronegativity: the ability of an atom in a molecule to attract electrons to itself. Electron affinity: the energy change for $\text{M}(g) + e^- \rightarrow \text{M}^-(g)$. Electron affinity deals with isolated atoms in the gas phase. **b.** Covalent bond: sharing of electron pair(s); polar covalent bond: unequal sharing of electron pair(s). **c.** Ionic bond: electrons are no longer shared, as in a covalent bond. Instead, there is a complete transfer of electron(s) from one atom to another to form ions. **15.** H_2O and NH_3 have lone pair electrons on the central atoms. These lone pair electrons require more space than the bonding electrons, which tends to compress the angles between the bonding pairs. The bond angle for H_2O is the smallest because oxygen has two lone pairs on the central atom and the bond angle is compressed more than in NH_3 , where N has only one lone pair. **17.** 1. polar bonds; 2. a structure such that the bond dipoles of the polar bonds do not cancel **19.** $(\text{NH}_4)_2\text{SO}_4$ and $\text{Ca}_3(\text{PO}_4)_2$ are compounds with both ionic and covalent bonds **21. a.** $\text{C} < \text{N} < \text{O}$; **b.** $\text{Se} < \text{S} < \text{Cl}$; **c.** $\text{Sn} < \text{Ge} < \text{Si}$; **d.** $\text{Ti} < \text{Ge} < \text{S}$ **23. a.** $\text{Ge}-\text{F}$; **b.** $\text{P}-\text{Cl}$; **c.** $\text{S}-\text{F}$; **d.** $\text{Ti}-\text{Cl}$ **25.** Order of electronegativity from Fig. 8.3: **a.** $\text{C}(2.5) < \text{N}(3.0) < \text{O}(3.5)$, same; **b.** $\text{Se}(2.4) < \text{S}(2.5) < \text{Cl}(3.0)$, same; **c.** $\text{Si} = \text{Ge} = \text{Sn}(1.8)$, different; **d.** $\text{Ti}(1.8) = \text{Ge}(1.8) < \text{S}(2.5)$, different. Most polar bonds using actual electronegativity values: **a.** $\text{Si}-\text{F}$ and $\text{Ge}-\text{F}$ equal polarity ($\text{Ge}-\text{F}$ predicted); **b.** $\text{P}-\text{Cl}$ (same as predicted); **c.** $\text{S}-\text{F}$ (same as predicted); **d.** $\text{Ti}-\text{Cl}$ (same as predicted) **27.** $\text{F}-\text{H} > \text{O}-\text{H} > \text{N}-\text{H} > \text{C}-\text{H} > \text{P}-\text{H}$ **29.** Rb^+ and Se^{2-} : $[\text{Ar}]4s^23d^{10}4p^6$; Ba^{2+} and I^- : $[\text{Kr}]5s^24d^{10}5p^6$ **31. a.** Sc^{3+} ; **b.** Te^{2-} ; **c.** Ce^{4+} , Ti^{4+} ; **d.** Ba^{2+} **33.** Some possibilities are N^{3-} , O^{2-} , F^- , Na^+ , Mg^{2+} , and Al^{3+} . $\text{Al}^{3+} < \text{Mg}^{2+} < \text{Na}^+ < \text{F}^- < \text{O}^{2-} < \text{N}^{3-}$ **35. a.** $\text{Cu} > \text{Cu}^+ > \text{Cu}^{2+}$; **b.** $\text{Pt}^{2+} > \text{Pd}^{2+} > \text{Ni}^{2+}$; **c.** $\text{O}^{2-} > \text{O}^- > \text{O}$; **d.** $\text{La}^{3+} > \text{Eu}^{3+} > \text{Gd}^{3+} > \text{Yb}^{3+}$; **e.** $\text{Te}^{2-} > \text{I}^- > \text{Cs}^+ > \text{Ba}^{2+} > \text{La}^{3+}$ **37. a.** Li_3N (lithium nitride); **b.** Ga_2O_3 (gallium oxide); **c.** RbCl (rubidium chloride); **d.** BaS (barium sulfide) **39. a.** NaCl , Na^+ smaller than K^+ ; **b.** LiF , F^- smaller than Cl^- ; **c.** MgO , O^{2-} greater charge than OH^- ; **d.** $\text{Fe}(\text{OH})_3$, Fe^{3+} greater charge than Fe^{2+} ; **e.** Na_2O , O^{2-} greater charge than Cl^- ; **f.** MgO , Mg^{2+} smaller than Ba^{2+} , and O^{2-} smaller than S^{2-} . **41.** $\Delta H_f^\circ = -412 \text{ kJ/mol}$ **43.** The lattice energy for $\text{Mg}^{2+}\text{O}^{2-}$ will be much more exothermic than for Mg^+O^- . **45.** Ca^{2+} has greater charge than Na^+ , and Se^{2-} is smaller than Te^{2-} . Since charge differences affect lattice energy values more than size differences, we expect the trend from most exothermic to least exothermic to be:



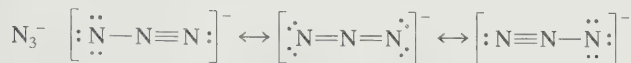
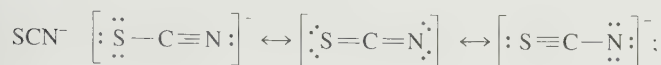
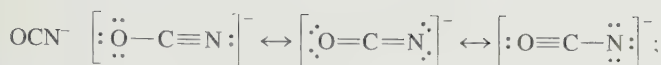
47. a. -183 kJ ; **b.** -109 kJ **49.** -42 kJ **51.** -1276 kJ **53.** 146 kJ/mol **55. a.** Using standard enthalpies of formation, $\Delta H^\circ = -184 \text{ kJ}$ vs. -183 kJ from bond energies; **b.** Using standard enthalpies of formation, $\Delta H = -92 \text{ kJ}$ vs. -109 kJ from bond energies. Bond energies give a reasonably good estimate for ΔH , especially when all reactants and products are gases. **57. a.** Using SF_4 data: $D_{\text{SF}} = 342.5 \text{ kJ/mol}$. Using SF_6 data: $D_{\text{SF}} = 327.0 \text{ kJ/mol}$. **b.** The $\text{S}-\text{F}$ bond energy in the table is 327 kJ/mol . The value in the table was based on the $\text{S}-\text{F}$ bond in SF_6 . **c.** $\text{S}(g)$ and $\text{F}(g)$ are not the most stable forms of the elements at 25°C . The most stable forms are $\text{S}_8(s)$ and $\text{F}_2(g)$; $\Delta H_f^\circ = 0$ for these two species. **59.** 388.2 kJ/mol vs. 391 kJ/mol in text



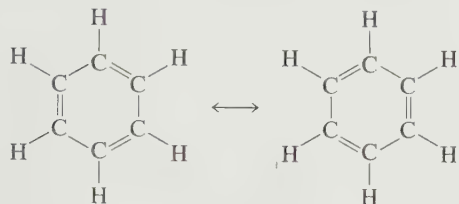
63.



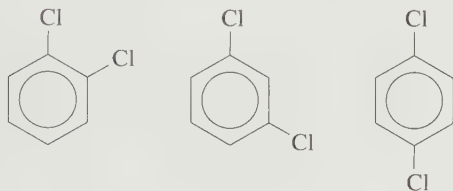
b.



67.



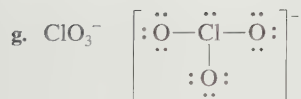
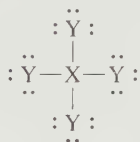
69. With resonance all carbon-carbon bonds are equivalent (we indicate this with a circle in the ring), giving three different structures:



Localized double bonds give four unique structures.

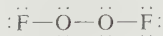
71. N_2 (triple bond) < N_2F_2 (double bond) < N_2F_4 (single bond)

73. **a**–**f**, and **h**. all have similar Lewis structures:



Formal charges: **a**. +1; **b**. +2; **c**. +3; **d**. +1; **e**. +2; **f**. +4; **g**. +2; **h**. +1

75.

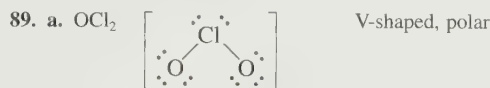


Formal charge: 0 0 0 0

Oxidation number: -1 +1 +1 -1

Oxidation numbers are more useful. We are forced to assign +1 as the oxidation number for oxygen. Oxygen is very electronegative and +1 is not a stable oxidation state for this element. 77. [61] **a**. linear, 180° ; **b**. trigonal pyramid, $<109.5^\circ$; **c**. tetrahedral, 109.5° ; **d**. tetrahedral, 109.5° ; **e**. trigonal planar, 120° ; **f**. V-shaped, $<109.5^\circ$; **g**. linear, 180° ; **h**. and **i**. linear, no bond angle in diatomic molecules; [65] **a**. NO_2 : V-shaped, $\sim 120^\circ$; NO_3^- : trigonal planar, 120° ; N_2O_4 : trigonal planar about both N atoms, 120° ; **b**. all are linear, 180° 79. Br_3^- : linear; ClF_3 and BrF_3 : T-shaped; SF_4 : see-saw 81. **a**. trigonal planar; 120° ; **b**. V-shaped; $\sim 120^\circ$ 83. **a**. linear, 180° ; **b**. T-shaped; $\sim 90^\circ$; **c**. see-saw; $\sim 90^\circ$ and $\sim 120^\circ$; **d**. trigonal bipyramid; 90° and 120° 85. SeO_2 (bond dipoles do not can-

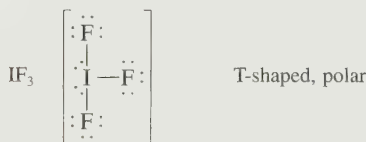
cel each other out in SeO_2) 87. ICl_3 and TeF_4 (bond dipoles do not cancel each other out in ICl_3 and TeF_4)



(one other resonance structure possible)



(Two other resonance structures possible)



91. Element E is a halogen (F, Cl, Br, or I); trigonal pyramid; $<109.5^\circ$

93. The polar bonds are symmetrically arranged about the central atoms, and all the individual bond dipoles cancel to give no net dipole moment

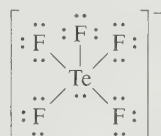
for each molecule, i.e., the molecules are nonpolar. **95. a.** radius: $N^+ < N < N^-$; I.E. $N^+ < N < N^-$; **b.** radius: $Cl^+ < Cl < Se < Se^-$; I.E. $Se^- < Se < Cl < Cl^+$; **c.** radius: $Sr^{2+} < Rb^+ < Br^-$; I.E. $Br^- < Rb^+ < Sr^{2+}$; **97. a.** 1549 kJ; **b.** 1390 kJ; **c.** 1312 kJ; **d.** 1599 kJ **99. a.** NaBr: In NaBr₂, the sodium ion would have a +2 charge assuming each bromine has a -1 charge. Sodium doesn't form stable Na²⁺ compounds. **b.** ClO₄⁻: ClO₄ has 31 valence electrons so it is impossible to satisfy the octet rule for all atoms in ClO₄. The extra electron from the -1 charge in ClO₄⁻ allows for complete octets for all atoms. **c.** XeO₄: We can't draw a Lewis structure that obeys the octet rule for SO₄ (30 electrons), unlike XeO₄ (32 electrons). **d.** SeF₄: Both compounds require the central atom to expand its octet. O is too small and doesn't have low-energy *d* orbitals to expand its octet (which is true for all row 2 elements).

101. The general structure of the trihalide ions is $\left[\ddot{X} - \ddot{X} - \ddot{X} \right]^-$. Bromine and iodine

are large enough and have low-energy, empty *d* orbitals to accommodate the expanded octet. Fluorine is small and its valence shell contains only 2*s* and 2*p* orbitals (4 orbitals) and cannot expand its octet. The *d* orbitals in F are 3*d*; they are too high in energy compared with 2*s* and 2*p* to be used.

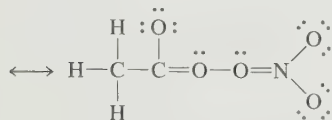
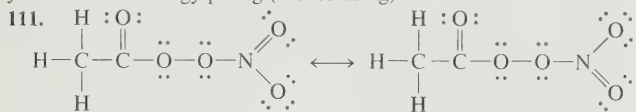
103. Yes, each structure has the same number of effective pairs around the central atom. (We count a multiple bond as a single group of electrons.)

105.

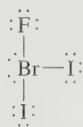


The lone pair of electrons around Te exerts a stronger repulsion than the bonding pairs. The stronger repulsion pushes the four square planar F atoms away from the lone pair, reducing the bond angles between the axial F atom and the square planar F atoms.

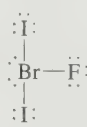
107. As the halogen atoms get larger, it becomes more difficult to fit three halogen atoms around the small nitrogen atom, and the NX₃ molecule becomes less stable. **109.** reaction i: -2636 kJ; reaction ii: -3471 kJ; reaction iii: -3543 kJ; Reaction iii yields the most energy per kg (-8085 kJ/kg)



113. a. Two possible structures exist; each has a T-shaped molecular structure:

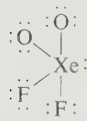


90° bond angle between I atoms

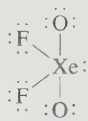


180° bond angle between I atoms

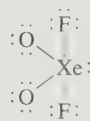
b. Three possible structures exist; each has a see-saw molecular structure.



90° bond angle
between O atoms

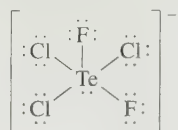


180° bond angle
between O atoms

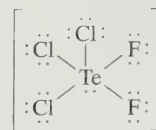


120° bond angle
between O atoms

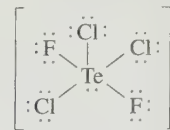
c. Three possible structures exist; each has a square pyramid molecular structure.



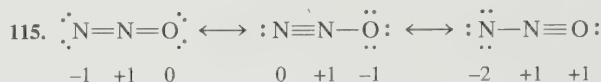
One F atom is 180°
from lone pair.



Both F atoms are 90°
from lone pair and 90°
from each other.



Both F atoms are 90°
from lone pair and 180°
from each other.

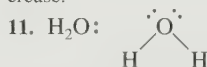


We should eliminate N—N≡O, since it has a formal charge of +1 on the most electronegative element (O). This is consistent with the observation that the N—N bond is between a double and triple bond and that the N—O bond is between a single and double bond.

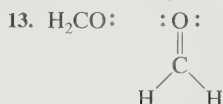
Chapter 9

7. Bond energy is proportional to bond order. Bond length is inversely proportional to bond order. Bond energy and length can be measured.

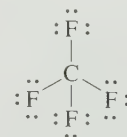
9. Paramagnetic: Unpaired electrons are present. Measure the mass of a substance in the presence and absence of a magnetic field. A substance with unpaired electrons will be attracted by the magnetic field, giving an apparent increase in mass in the presence of the field. Greater numbers of unpaired electrons will give greater attraction and greater observed mass increase.



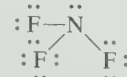
H₂O has a tetrahedral arrangement of the electron pairs about the O atom that requires *sp*³ hybridization. Two of the *sp*³ hybrid orbitals are used to form bonds to the two hydrogen atoms, and the other two *sp*³ hybrid orbitals hold the two lone pairs on oxygen.



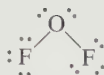
The central carbon atom has a trigonal planar arrangement of the electron pairs that requires *sp*² hybridization. Two of the *sp*² hybrid orbitals are used to form the two bonds to hydrogen. The other *sp*² hybrid orbital forms the σ bond to oxygen. The unchanged (unhybridized) *p* orbital on carbon is used to form the π bond between carbon and oxygen. **15. [61] a.** *sp*; **b.** *sp*³; **c.** *sp*³; **d.** *sp*³; **e.** *sp*²; **f.** *sp*³; **g.** *sp*; **h.** each O is *sp*² hybridized; **i.** Br is *sp*³ hybridized [65] **a.** NO₂⁻, *sp*²; NO₃⁻, *sp*²; N₂O₄: both N atoms are *sp*² hybridized; **b.** All are *sp* hybridized. **17.** PF₅, *dsp*³; BeH₂, *sp*; BH₃, *sp*²; Br₃⁻, *dsp*³; SF₄, *dsp*³; XeF₄, *d*²*sp*³; ClF₅, *d*²*sp*³; SF₆, *d*²*sp*³ **19.** The molecules in Exercise 81 all exhibit *sp*² hybridization about the central atom; the molecules in Exercise 82 all exhibit *sp*³ hybridization about the central atom. **21. a.** tetrahedral, 109.5°, *sp*³, nonpolar



b. trigonal pyramid, <109.5°, *sp*³, polar



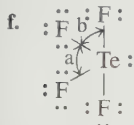
- c. V-shaped, $<109.5^\circ$, sp^3 , polar



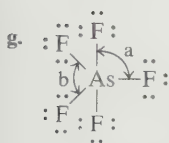
- d. trigonal planar, 120° , sp^2 , nonpolar



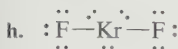
- e. linear, 180° , sp , nonpolar



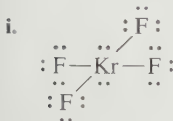
- a $\approx 120^\circ$, see-saw, dsp^3 , polar
b $\approx 90^\circ$



- a = 90° , trigonal bipyramid, dsp^3 , nonpolar
b = 120°



- linear, 180° , dsp^3 , nonpolar



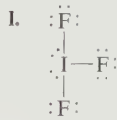
- square planar, 90° , d^2sp^3 , nonpolar



- octahedral, 90° , d^2sp^3 , nonpolar

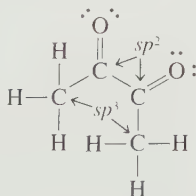


- square pyramid, $\approx 90^\circ$;
 d^2sp^3 , polar

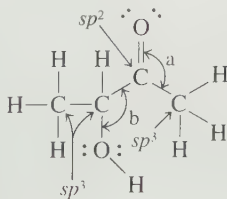


- T-shaped, $\approx 90^\circ$;
 dsp^3 , polar

23. The π bond forces all six atoms into the same plane. 25. Biacetyl

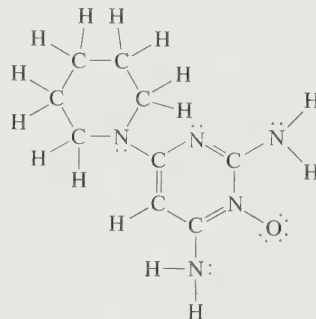


All CCO angles are 120° . The six atoms are not in the same plane. 11σ and 2π
Acetoin



angle a = 120° , angle b = 109.5° , 13 σ and 1 π bond 27. To complete the Lewis structure, add lone pairs to complete octets for each atom. a. 6; b. 4; c. The center N in $-\text{N}=\text{N}=\text{N}$ group; d. 33 σ ; e. 5 π ; f. 180° ; g. $<109.5^\circ$; h. sp^3

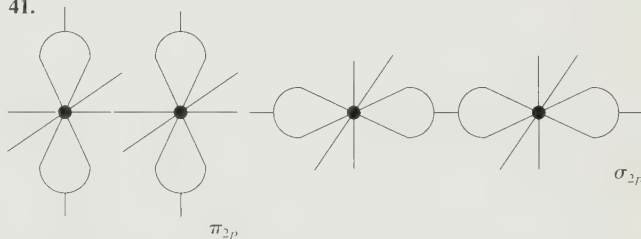
29.



a. The two nitrogens in the ring with double bonds are sp^2 hybridized. The other three nitrogens are sp^3 hybridized. b. The five carbon atoms in the ring with one nitrogen are all sp^3 hybridized. The four carbon atoms in the other ring with double bonds are all sp^2 hybridized. c. Angles a and b: $\approx 109.5^\circ$; angles c, d, and e: $\approx 120^\circ$; d. 31 σ bonds; e. 3 π bonds

31. a. H_2^+ , H_2 , H_2^- ; b. He_2^{2+} and He_2^+ 33. a. $(\sigma_{2s})^2$; B.O. = 1; diamagnetic (0 unpaired electrons); b. $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4$; B.O. = 2; diamagnetic (0 unpaired electrons); c. $(\sigma_{3s})^2(\sigma_{3s}^*)^2(\sigma_{3p})^2(\pi_{3p})^4(\pi_{3p}^*)^2$; B.O. = 2; paramagnetic (2 unpaired electrons) 35. O_2^+ : $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^1$; B.O. = 2.5; 1 unpaired electron; O_2 : $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^2$; B.O. = 2; 2 unpaired electrons; O_2^- : $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^3$; B.O. = 1.5; 1 unpaired electron; O_2^{2-} : $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^4$; B.O. = 1; 0 unpaired electrons; bond energy: $\text{O}_2^{2-} < \text{O}_2^- < \text{O}_2 < \text{O}_2^+$; bond length: $\text{O}_2^+ < \text{O}_2 < \text{O}_2^- < \text{O}_2^{2-}$ 37. a. $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^2$; B.O. = 3; diamagnetic; b. $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^1$; B.O. = 2.5; paramagnetic; c. $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4$; B.O. = 2; diamagnetic; bond length: $\text{CO} < \text{CO}^+ < \text{CO}^{2+}$; bond energy: $\text{CO}^{2+} < \text{CO}^- < \text{CO}$ 39. H_2 ; N_2

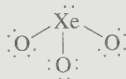
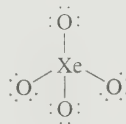
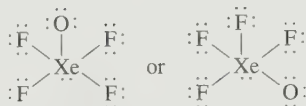
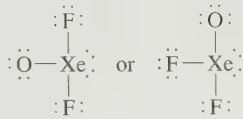
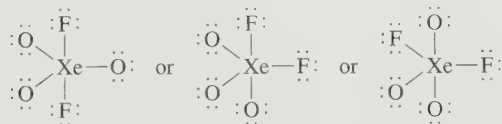
41.



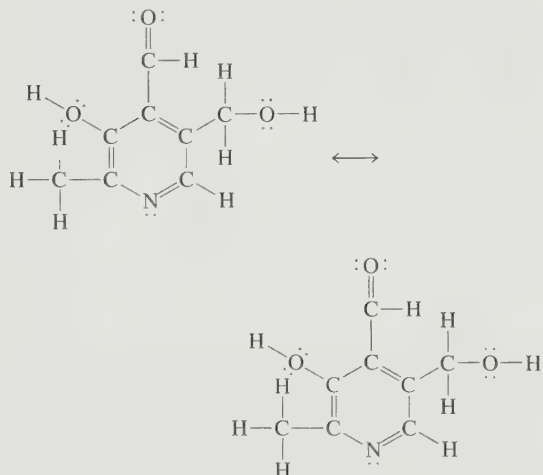
43. a. The electrons would be closer to F on the average. The F atom is more electronegative than the H atom, and the $2p$ orbital of F is lower in energy than the $1s$ orbital of H; b. The bonding MO would have more fluorine $2p$ character because it is closer in energy to the fluorine $2p$ orbital; c. The antibonding MO would place more electron density closer to H and would have a greater contribution from the higher-energy hydrogen $1s$ atomic orbital. 45. O_3 and NO_2^- have identical Lewis structures, so we need to discuss only one of them. The Lewis structure for O_3 is



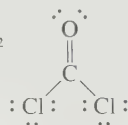
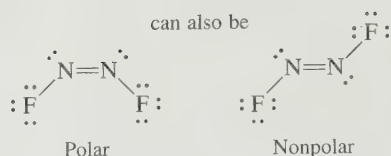
Localized electron model: The central oxygen atom is sp^2 hybridized, which is used to form the two σ bonds and hold the lone pair of electrons. An unchanged (unhybridized) p atomic orbital forms the π bond with the neighboring oxygen atoms. The π bond resonates between the two positions. Molecular orbital model: There are two localized σ bonds and a π bond that is delocalized over the entire surface of the molecule. The delocalized π bond results from overlap of a p atomic orbital on each oxygen atom in O_3 .

47. a. Trigonal pyramid; sp^3 b. Tetrahedral; sp^3 c. See-saw; dsp^3 d. T-shaped; dsp^3 e. Trigonal bipyramid; dsp^3 

49.

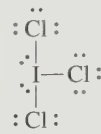


a. 20 σ bonds; 4 π bonds (The electrons in the 3 π bonds in the ring are delocalized.) b. angles a, c, and g: $\approx 109.5^\circ$; angles b, d, e, and f: $\approx 120^\circ$; c. 6 sp^2 carbons; d. 4 sp^3 atoms; e. Yes, the π electrons in the ring are delocalized. The atoms in the ring are all sp^2 hybridized. This leaves a p orbital perpendicular to the plane of the ring from each atom. Overlap of all six of these p orbitals results in a π molecular orbital system where the electrons are delocalized above and below the plane of the ring (similar to benzene in Fig. 9.48 of the text).

51. a. COCl_2 Trigonal planar, polar, 120° , sp^2 b. N_2F_2 V-shaped about both N atoms, $\approx 120^\circ$, sp^2

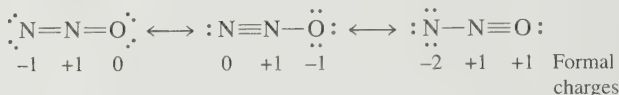
These are distinctly different molecules.

c. COS

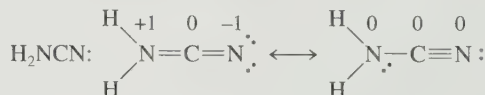
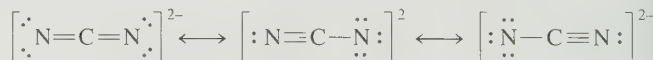
d. ICl_3 T-shaped, polar, $\approx 90^\circ$, dsp^3

53. a. The NNO structure is correct. From the Lewis structures we would predict both NNO and NON to be linear, but NON would be nonpolar. NNO is polar.

b.

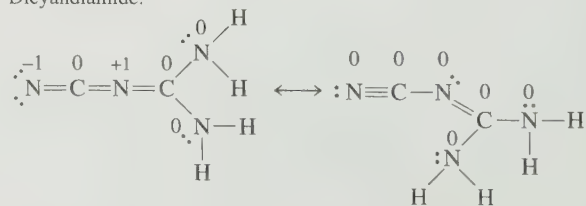


The central N is sp hybridized. We can probably ignore the third resonance structure on the basis of formal charge. c. sp hybrid orbitals on the center N overlap with atomic orbitals (or hybrid orbitals) on the other two atoms to form two σ bonds. The remaining p orbitals on the center N overlap with p orbitals on the other N to form two π bonds. 55. N_2 : $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^2$ in ground state, B.O. = 3, diamagnetic; 1st excited state: $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^1(\pi_{2p}^*)^1$, B.O. = 2, paramagnetic (two unpaired electrons) 57. F_2 $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^4$; F_2 should have a lower ionization energy than F. The electron removed from F_2 is in a π_{2p}^* antibonding molecular orbital, which is higher in energy than the $2p$ atomic orbitals from which the electron in atomic fluorine is removed. Since the electron removed from F_2 is higher in energy than the electron removed from F, then it should be easier to remove an electron from F_2 than from F. 59. a. No, some atoms are attached differently; b. Structure 1: All N = sp^3 , all C = sp^2 ; structure 2: All C and N = sp^2 ; c. The first structure with the carbon-oxygen double bonds is slightly more stable.

61. a. NCN^{2-} :

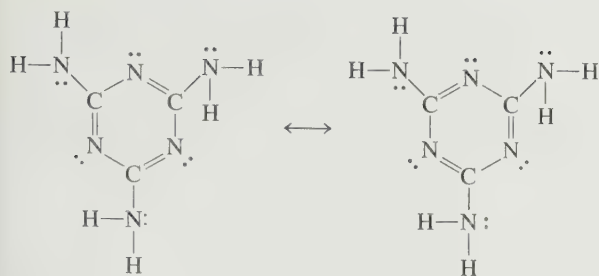
Favored by formal charge

Dicyandiamide:

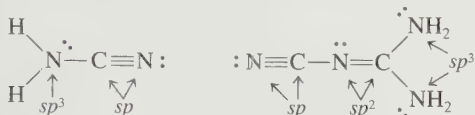


Favored by formal charge

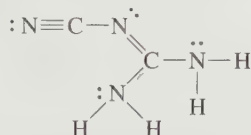
Melamine:



b. NCN^{2-} : C is sp hybridized. Cannot predict hybrids for N's (different for each resonance structure). For the remaining compounds, we will predict hybrids for the favored resonance structures only.



Melamine: N in NH_2 groups are all sp^3 hybridized. Atoms in ring are all sp^2 hybridized; c. NCN^{2-} : 2 σ and 2 π bonds; H_2NCN : 4 σ and 2 π bonds; dicyandiamide: 9 σ and 3 π bonds; melamine: 15 σ and 3 π bonds; d. The π system forces the ring to be planar just as the benzene ring is planar. e. The structure



is the most important because it has three different CN bonds. This structure is also favored on the basis of formal charge. 63. a. 25-nm light has sufficient energy to ionize N and N_2 and to break the triple bond in N_2 . Thus, N_2 , N_2^+ , N, and N^+ will all be present, assuming excess N_2 . b. $85.33 \text{ nm} < \lambda \leq 127 \text{ nm}$; c. The ionization energy of a substance is the energy it takes to completely remove an electron. N_2 : $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p})^4(\sigma_{2p})^2$; the electron removed from N_2 is in the σ_{2p} molecular orbital, which is lower in energy than the $2p$ atomic orbital from which the electron in atomic nitrogen is removed. Since the electron removed from N_2 is lower in energy than the electron removed in N, then the ionization energy of N_2 is greater than the ionization energy of N. 65. Both reactions apparently involve only the breaking of the N—Cl bond. However, in the reaction $\text{ONCl} \rightarrow \text{NO} + \text{Cl}$ some energy is released in forming the stronger NO bond, lowering the value of ΔH . Therefore, the apparent N—Cl bond energy is artificially low for this reaction. The first reaction involves only the breaking of the N—Cl bond. 67. a. The CO bond is polar, with the negative end around the more electronegative oxygen atom. We would expect metal cations to be attracted to and to bond to the oxygen end of CO on the basis of electronegativity. b. The formal charge on C is -1 , and the formal charge on O is $+1$. From formal charge, we would expect metal cations to bond to the carbon (with the negative formal charge.) c. In molecular orbital theory, only orbitals with proper symmetry overlap to form bonding orbitals. The metals that form bonds to CO are usually transition metals, all of which have outer electrons in the d orbitals. The only molecular orbitals of CO that have proper symmetry to overlap with d orbitals are the π_{2p}^* orbitals, whose shape is similar to that of the d orbitals (see Fig. 9.34). Since the antibonding molecular orbitals have more carbon character, one would expect the bond to form through carbon.

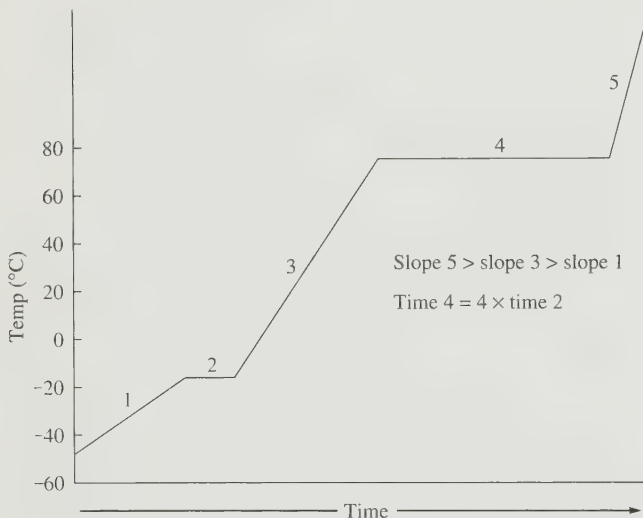
Chapter 10

13. London dispersion forces (LD forces) $<$ dipole–dipole $<$ H bonding $<$ metallic bonding, covalent network, ionic. Yes, there is considerable overlap. Consider some of the examples in Exercise 10.92. Benzene (only

LD forces) has a higher boiling point than acetone (dipole–dipole). Also, there is even more overlap of the stronger forces (metallic, covalent, and ionic). 15. a. *Polarizability* of an atom refers to the ease of distorting the electron cloud. It also can refer to distorting the electron clouds in molecules or ions. *Polarity* refers to the presence of a permanent dipole moment in a molecule. b. London dispersion forces are present in all substances. LDF can be referred to as accidental dipole-induced dipole forces. Dipole–dipole forces involve the attraction of molecules with permanent dipoles for each other. c. *inter*: between; *intra*: within. For example, in Br_2 the covalent bond is an intramolecular force, holding the two Br atoms together in the molecule. The much weaker London dispersion forces are intermolecular forces of attraction, which hold different Br_2 molecules together in the liquid phase. 17. Atoms have an approximately spherical shape. It is impossible to pack spheres together without some empty space between the spheres. 19. As the intermolecular forces increase, the critical temperature increases. 21. a. crystalline solid: long range order; amorphous solid: no long range order; b. ionic solid: contains ions held together by ionic bonding; molecular solid: contains discrete covalently bonded molecules held together in the solid by weaker forces (LDF, dipole, or hydrogen bonds); c. molecular solid: discrete molecules; covalent network solid: no discrete molecules. A covalent network is like a giant molecule. The intermolecular forces are the covalent bonds between the atoms. d. metallic solid: contains delocalized electrons; excellent conductor of electricity; covalent network: localized electrons, insulator or semiconductor 23. *Conductor*: The energy difference between the filled and unfilled molecular orbitals is minimal. We call this energy difference the band gap. Since the band gap is minimal, electrons can easily move into the conduction bands (the unfilled molecular orbitals). *Insulator*: Large band gap. Electrons do not move from the filled molecular orbitals to the conduction bands since the energy difference is large. *Semiconductor*: Small band gap. Since the energy difference between the filled and unfilled molecular orbitals is smaller than in insulators, some electrons can jump into the conduction bands. The band gap, is not as small as with conductors, so semiconductors have intermediate conductivity. a. As the temperature is increased, more electrons in the filled molecular orbitals have sufficient kinetic energy to jump into the conduction bands (the unfilled molecular orbitals). b. A photon of light is absorbed by an electron, which then has sufficient energy to jump into the conduction bands. c. An impurity either adds electrons at an energy near that of the conduction bands (n-type) or creates holes (unfilled energy levels) at energies in the previously filled molecular orbitals (p-type). 25. Ge doped with P or As would produce an n-type semiconductor, and Ge doped with Ga or In would produce a p-type semiconductor. 27. a. condensation: vapor $\rightarrow$ liquid; b. evaporation: liquid $\rightarrow$ vapor; c. sublimation: solid $\rightarrow$ vapor; d. A supercooled liquid is a liquid at a temperature below its freezing point. 29. a. As intermolecular forces increase, the rate of evaporation decreases. b. increase T : increase rate; c. increase surface area: increase rate 31. $\text{C}_2\text{H}_5\text{OH}(l) \rightarrow \text{C}_2\text{H}_5\text{OH}(g)$ is an endothermic process. Heat is absorbed when liquid ethanol vaporizes; the internal heat from the body provides this heat. 33. The phase change, $\text{H}_2\text{O}(g) \rightarrow \text{H}_2\text{O}(l)$ releases heat that can cause additional damage. Also steam can be at a temperature much greater than 100°C . 35. a. LD (London dispersion); b. dipole, LD; c. hydrogen bonding, LD; d. ionic; e. LD; f. dipole, LD; g. ionic 37. a. OCS; b. SO_2 ; c. $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$; d. H_2CO ; e. CH_3OH 39. a. HCl has dipole forces in addition to LD forces; b. NaCl, stronger ionic forces; c. I_2 , larger molecule so stronger LD forces; d. N_2 , smallest nonpolar compound present, has weakest LD forces; e. CH_4 , smallest nonpolar compound present, has weakest LD forces; f. HF, can form relatively strong hydrogen bonding interactions, unlike the other compounds; g. $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$, unlike others, has relatively strong hydrogen bonding. 41. H_2O is attracted to glass while Hg is not. 43. The structure of H_2O_2 produces greater hydrogen bonding than water. Long chains of hydrogen bonded H_2O_2 molecules then get tangled together. 45. $3.13 \text{ \AA}$ 47. 1.54

g/cm³ **49.** 22.68 g/cm³ **51.** edge, 328 pm; radius, 142 pm **53.** For a cubic closest packed structure, 74.06% of the volume of each unit cell is occupied by atoms; in a simple cubic unit cell structure, 52.36% is occupied. The cubic (and hexagonal) closest packed structures provide the most efficient means for packing atoms. **55.** p-type **57.** 5.0×10^2 nm **59.** NaCl: 4Na⁺, 4Cl⁻; CsCl: 1Cs⁺, 1Cl⁻; ZnS: 4Zn²⁺, 4S²⁻; TiO₂: 2Ti⁴⁺, 4O²⁻ **61.** CoF₂ **63.** MF₂ **65.** From density data, 421 pm; from ionic radii data, 410. pm; the two values agree within 3%. **67.** **a.** CO₂: molecular; **b.** SiO₂: covalent network; **c.** Si: atomic, covalent network; **d.** CH₄: molecular; **e.** Ru: atomic, metallic; **f.** I₂: molecular; **g.** KBr: ionic; **h.** H₂O: molecular; **i.** NaOH: ionic; **j.** U: atomic, metallic; **k.** CaCO₃: ionic; **l.** PH₃: molecular **69.** **a.** The unit cell consists of Ni at the cube corners and Ti at the body center or Ti at the cube corners and Ni at the body center. **b.** NiTi: **c.** Both have a coordination number of 8. **71.** CaTiO₃; six oxygens around each Ti **73.** **a.** YBa₂Cu₃O₉; **b.** The structure of this superconductor material is based on the second perovskite structure. The YBa₂Cu₃O₉ structure is three of these cubic perovskite unit cells stacked on top of each other. The oxygen atoms are in the same places, Cu takes the place of Ti, and two Ca atoms are replaced by Ba and one Ca atom is replaced by Y. **c.** YBa₂Cu₃O₇ **75.** Li, 158 kJ/mol; Mg, 139 kJ/mol. Bonding is stronger in Li. **77.** 89°C **79.** 2.56×10^{-3} torr

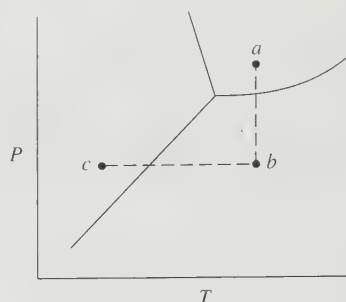
81.



83. 1680 kJ **85.** 1490 g **87.** A: solid; B: liquid; C: vapor; D: solid + vapor; E: solid + liquid + vapor (triple point); F: liquid + vapor; G: liquid + vapor (critical point); H: vapor; the first dashed line (at the lower temperature) is the normal melting point, and the second dashed line is the normal boiling point. The solid phase is denser. **89.** **a.** two; **b.** higher pressure triple point: graphite, diamond, and liquid; lower pressure triple point: graphite, liquid and vapor; **c.** It is converted to diamond (the more dense solid form); **d.** Diamond is more dense, which is why graphite can be converted to diamond by applying pressure. **91.** C₂₅H₅₂ has the stronger intermolecular forces because it has the higher boiling point. Even though C₂₅H₅₂ is nonpolar, it is so large that its London dispersion forces are much stronger than the sum of the London dispersion forces and hydrogen bonding interactions found in H₂O. **93.** A: CH₄; B: SiH₄ C: NH₃ **95.** 0.229 nm **97.** If TiO₂ conducts electricity as a liquid, then it would be ionic. **99.** B₂H₆, molecular; SiO₂, network; CsI, ionic; W, metallic **101.** 4.65 kg/h **103.** 46.7 kJ/mol; 90% **105.** The solids with high melting points (NaCl, MgCl₂, NaF, MgF₂, AlF₃) are all ionic solids. SiCl₄, SiF₄, Cl₂, F₂, PF₅, and SF₆ are nonpolar covalent molecules with LD

forces. PCl₃ and SCl₂ are polar molecules with LD and dipole forces. In these 8 molecular substances the intermolecular forces are weak and the melting points low. AlCl₃ is intermediate. The melting point indicates there are stronger forces present than in the nonmetal halides, but not as strong as for an ionic solid. AlCl₃ illustrates a gradual transition from ionic to covalent bonding; from an ionic solid to discrete molecules. **107.** TiO_{1.182} or Ti_{0.8462} O; 63.7% Ti²⁺, 36.3% Ti³⁺ **109.** 6.58 g/cm³

111.



As *P* is lowered, we go from *a* to *b* on the phase diagram. The water boils. The evaporation of the water is endothermic and the water is cooled (*b* → *c*), forming some ice. If the pump is left on, the ice will sublime until none is left. This is the basis of freeze drying.

Chapter 11

9. 0.365 *M* **11.** 1.54×10^{-2} *M* NiCl₂, Ni²⁺: 1.54×10^{-2} *M*; Cl⁻: 3.08×10^{-2} *M* **13.** Since volume is temperature-dependent and mass is not, then molarity is temperature-dependent and molality is temperature-independent. In determining Δ*T*_f and Δ*T*_b, we are interested in how some temperature depends on composition. Thus we do not want our expression of composition to also be dependent on temperature. **15.** Hydrophobic: water hating; hydrophilic: water loving **17.** The levels of the liquids in each beaker will become constant when the concentration of solute is the same in both beakers. Since A is less volatile, the beaker on the right will have a larger volume when the concentrations become equal. Water will initially condense in this beaker in a larger amount than solute is evaporating, while the net change occurring initially in the other beaker is for water to evaporate in a larger amount than solute is condensing. Eventually the rate that solute and H₂O leave and return to each beaker will become equal when the concentrations become equal. **19.** No. For an ideal solution, Δ*H*_{soln} = 0 **21.** The osmotic pressure inside bacteria cells is less than outside the cell causing the cells to dehydrate and die. **23.** The Tyndall effect is the scattering of light by particles. Colloids scatter light, and true solutions do not scatter light. **25.** 2.5%; 0.43 *M*; 0.44 *m*; 7.9×10^{-3} **27.** HCl: 12 *M*, 17 *m*, 0.23; HNO₃: 16 *M*, 37 *m*, 0.39; H₂SO₄: 18 *M*, 200 *m*, 0.76; HC₂H₃O₂: 17 *M*, 2000 *m*, 0.96; NH₃: 15 *M*, 23 *m*, 0.29 **29.** 35%; 0.39; 7.3 *m*; 3.1 *M* **31.** 23.9%; 1.6 *m*, 0.028, 4.11 *N* **33.** NaI(*s*) → Na⁺(*aq*) + I⁻(*aq*) Δ*H*_{soln} = -8 kJ/mol **35.** The attraction of water molecules for Al³⁺ and OH⁻ cannot overcome the larger lattice energy of Al(OH)₃. **37.** Water will dissolve polar solutes (*c* and *d*) and ionic solutes (*b*). Carbon tetrachloride will dissolve nonpolar solutes (*a* and *e*). **39.** Ability to form hydrogen bonding interactions, ability to break up into ions, and polarity are some factors affecting solute solubility. **a.** CH₃CH₂OH; **b.** CHCl₃; **c.** CH₃CH₂OH **41.** As the length of the hydrocarbon chain increases, the solubility decreases because the nonpolar hydrocarbon chain interacts poorly with the polar water molecules. **43.** 1.04×10^{-3} mol/L · atm; 1.14×10^{-3} mol/L **45.** 23.6 torr **47.** 3.0×10^2 g/mol **49.** **a.** 290 torr; **b.** 0.69 **51.** *X*_{methanol} = *X*_{propanol} = 0.500 **53.** solution *c* **55.** *P*_{ideal} = 188.6 torr; *X*_{acetone} = 0.512, *X*_{methanol} = 0.488; since the actual vapor pressure of the solution is smaller than the ideal vapor pressure, then this solution exhibits a negative deviation from Raoult's law. This occurs when solute-solvent attractions are stronger than for the pure substances. **57.** 100.042°C **59.** 14.8 g C₃H₈O₃ **61.** *T*_f = -29.9°C, *T*_b = 108.2°C

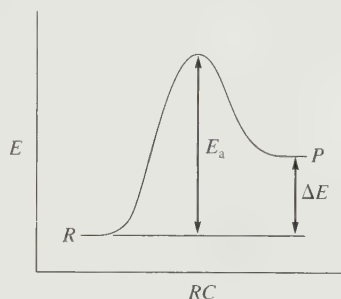
63. 456 g/mol **65. a.** $\Delta T = 2.0 \times 10^{-5}^\circ\text{C}$, $\pi = 0.20$ torr; **b.** Osmotic pressure is better for determining the molar mass of large molecules. A temperature change of 10^{-5}°C is very difficult to measure. A change in height of a column of mercury by 0.2 mm is not as hard to measure precisely. **67.** 0.327 *M* **69. a.** 0.010 *m* Na_3PO_4 and 0.020 *m* KCl ; **b.** 0.020 *m* HF ; **c.** 0.020 *m* CaBr_2 **71. a.** $T_f = -0.28^\circ\text{C}$; $T_b = 100.077^\circ\text{C}$; **b.** $T_f = -0.37^\circ\text{C}$; $T_b = 100.10^\circ\text{C}$ **73.** 2.63 (0.0225 *m*), 2.60 (0.0910 *m*), 2.57 (0.278 *m*); $i_{\text{average}} = 2.60$ **75.** 37 atm; the osmotic pressure should be lower due to ion pairing. **77. a.** 26.6 kJ/mol; **b.** -657 kJ/mol **79. a.** Water boils when the vapor pressure equals the pressure above the water. In an open pan, $P_{\text{atm}} \approx 1.0$ atm. In a pressure cooker, $P_{\text{inside}} > 1.0$ atm and water boils at a higher temperature. The higher the cooking temperature, the faster the cooking time. **b.** Salt dissolves in water, forming a solution with a melting point lower than that of pure water ($\Delta T_f = K_f m$). This happens in water on the surface of ice. If it is not too cold, the ice melts. This process won't occur if the ambient temperature is lower than the depressed freezing point of the salt solution. **c.** When water freezes from a solution, it freezes as pure water, leaving behind a more concentrated salt solution. **d.** On the CO_2 phase diagram, the triple point is above 1 atm and $\text{CO}_2(\text{g})$ is the stable phase at 1 atm and room temperature. $\text{CO}_2(\text{l})$ can't exist at normal atmospheric pressures, which explains why dry ice sublimates rather than boils. In a fire extinguisher, $P > 1$ atm and $\text{CO}_2(\text{l})$ can exist. When CO_2 is released from the fire extinguisher, $\text{CO}_2(\text{g})$ forms as predicted from the phase diagram. **e.** Adding a solute to a solvent increases the boiling point and decreases the freezing point of the solvent. Thus, the solvent is a liquid over a wider range of temperatures when a solute is dissolved. **81.** 0.600 **83.** $\text{C}_2\text{H}_4\text{O}_6$; 151 g/mol (exp.); 152.10 g/mol (calc.); $\text{C}_4\text{H}_8\text{O}_6$ **85.** 1.97% NaCl **87.** 0.050 **89.** 44% naphthalene, 56% anthracene **91.** -0.20°C , 100.056°C **93. a.** 46 L; **b.** No; A reverse osmosis system that applies 8.0 atm can purify only water with solute concentrations less than 0.32 mol/L. Salt water has a solute concentration of $2(0.60\text{ M}) = 1.2\text{ M}$ ions. The solute concentration of salt water is much too high for this reverse osmosis unit to work.

Chapter 12

9. For a generic reaction $\text{A} \rightarrow \text{B}$, an instantaneous rate is the slope of a tangent line to the graph of $[\text{A}]$ versus time (or $[\text{B}]$ versus time). We can determine an instantaneous rate at any time. The instantaneous rate at $t \approx 0$ is called the *initial rate*. Since a tangent line generally has the greatest slope at $t \approx 0$ versus tangent lines at other times, then the initial rate would have the largest rate value. The average rate is the change in concentration of a reactant or product per some time period ($\Delta[\text{A}]/\Delta t$); an average rate is determined over some time period while an instantaneous rate is determined at one specific time. **11. a.** The greater the frequency of collisions, the greater the opportunity for molecules to react, and hence the greater the rate. **b.** Chemical reactions involve the making and breaking of chemical bonds. The kinetic energy of the collisions can be used to break bonds. So, as the kinetic energy of the collisions increases, the rate increases. **c.** For a reaction to occur, it is the reactive portion of each molecule that must be involved in a collision. Only some of all the possible collisions have the correct orientation to convert from reactants to products. **13.** A catalyst increases the rate of a reaction by providing reactants with an alternate pathway (mechanism) to convert to products. This alternate pathway has a lower activation energy, increasing the rate of reaction. A homogeneous catalyst is in the same phase as the reactants. A heterogeneous catalyst is in a different phase than the reactants. The catalyst is usually a solid, although a catalyst in a liquid phase can act as a heterogeneous catalyst for some gas-phase reactions. No, the catalyzed reaction has a different mechanism and hence, most likely, a different rate law. **15. a.** They are independent of each other. **b.** The rate law can be determined only from experiment. **c.** Most reactions occur by a multiple series of steps. **17.** P_4 : 6.0×10^{-4} mol/L $\cdot$ s; H_2 : 3.6×10^{-3} mol/L $\cdot$ s **19. a.** mol/L $\cdot$ s;

b. mol/L $\cdot$ s; **c.** s^{-1} ; **d.** L/mol $\cdot$ s; **e.** $\text{L}^2/\text{mol}^2 \cdot \text{s}$ **21. a.** rate = $k[\text{NO}]^2[\text{Cl}_2]$; **b.** $1.8 \times 10^2 \text{ L}^2/\text{mol}^2 \cdot \text{min}$ **23. a.** rate = $k[\text{NOCl}]^2$; **b.** $6.6 \times 10^{-29} \text{ cm}^3/\text{molecules} \cdot \text{s}$; **c.** $4.0 \times 10^{-8} \text{ L/mol} \cdot \text{s}$ **25. a.** first order in Hb and first order in CO ; **b.** rate = $k[\text{Hb}][\text{CO}]$; **c.** 0.280 L/mol $\cdot$ s; **d.** 2.26 $\mu\text{mol/L} \cdot \text{s}$ **27.** rate = $k[\text{H}_2\text{O}_2]$; $\ln[\text{H}_2\text{O}_2] = -kt + \ln[\text{H}_2\text{O}_2]_0$; $k = 8.3 \times 10^{-4} \text{ s}^{-1}$; 0.037 *M* **29.** rate = $k[\text{NO}_2]^2$; $\frac{1}{[\text{NO}_2]} = kt + \frac{1}{[\text{NO}_2]_0}$; $k = 2.08 \times 10^{-4} \text{ L/mol} \cdot \text{s}$; 0.131 *M* **31. a.** rate = k ; $[\text{C}_2\text{H}_5\text{OH}] = -kt + [\text{C}_2\text{H}_5\text{OH}]_0$; since slope = $-k$, then $k = 4.00 \times 10^{-5} \text{ mol/L} \cdot \text{s}$; **b.** 156 s; **c.** 313 s **33.** rate = $k[\text{C}_4\text{H}_6]^2$; $\frac{1}{[\text{C}_4\text{H}_6]} = kt + \frac{1}{[\text{C}_4\text{H}_6]_0}$; $k = 1.4 \times 10^{-2} \text{ L/mol} \cdot \text{s}$ **35.** second order; 0.1 *M* **37. a.** $[\text{A}] = -kt + [\text{A}]_0$; **b.** $1.0 \times 10^{-2} \text{ s}$; **c.** $2.5 \times 10^{-4} \text{ M}$ **39. a.** $1.01 \times 10^{-3} \text{ s}^{-1}$; **b.** 686 s; **c.** 280 s (25%); $1.4 \times 10^3 \text{ s}$ (75%); $3 \times 10^3 \text{ s}$ (95%) **41.** 0.12 L/mol $\cdot$ s **43. a.** $1.1 \times 10^{-3} \text{ M}$; **b.** 0.025 *M* **45. a.** rate = $k[\text{CH}_3\text{NC}]$; **b.** rate = $k[\text{O}_3][\text{NO}]$; **c.** rate = $k[\text{O}_3]$; **d.** rate = $k[\text{O}_3][\text{O}]$ **47.** Rate = $k[\text{C}_4\text{H}_9\text{Br}]$; $\text{C}_4\text{H}_9\text{Br} + 2\text{H}_2\text{O} \rightarrow \text{C}_4\text{H}_9\text{OH} + \text{Br}^- + \text{H}_3\text{O}^+$; the intermediates are C_4H_9^+ and $\text{C}_4\text{H}_9\text{OH}_2^+$.

49.



51. 341 kJ/mol **53.** The graph of $\ln k$ versus $1/T$ is linear with slope = $-E_a/R = -1.2 \times 10^4 \text{ K}$; $E_a = 1.0 \times 10^2 \text{ kJ/mol}$ **55.** $4.8 \times 10^3 \text{ s}^{-1}$ **57.** 51°C **59.** $\text{H}_3\text{O}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l})$ should have the faster rate. H_3O^+ and OH^- will be electrostatically attracted to each other; Ce^{4+} and Hg_2^{2+} will repel each other (so E_a is much larger). **61. a.** NO; **b.** NO_2 ; **c.** 2.3 **63.** $\text{CH}_3\text{D}-\text{CH}_2\text{D}$ should be the product. If the mechanism is possible, then the reaction must be $\text{C}_2\text{H}_4 + \text{D}_2 \rightarrow \text{CH}_2\text{DCH}_2\text{D}$. If we got this product, then we could conclude that this is a possible mechanism. If we got some other product, e.g., CH_3CHD_2 , then we would conclude that the mechanism is wrong. Even though this mechanism correctly predicts the products of the reaction, we cannot say conclusively that this is the correct mechanism; we might be able to conceive of other mechanisms that would give the same product as our proposed one. **65.** $5.68 \times 10^{18} \text{ molecules/cm}^3 \cdot \text{s}$ **67.** $1.0 \times 10^2 \text{ kJ/mol}$ **69.** At high $[\text{S}]$, the enzyme is completely saturated with substrate. Once the enzyme is completely saturated, the rate of decomposition of ES can no longer increase, and the overall rate remains constant. **71.** rate = $\frac{k[\text{I}^-][\text{OCl}^-]}{[\text{OH}^-]}$; $k = 6.0 \times 10^1 \text{ s}^{-1}$ **73. a.** first order with respect to both reactants; **b.** rate = $k[\text{NO}][\text{O}_3]$; **c.** $k' = 1.8 \text{ s}^{-1}$; $k'' = 3.6 \text{ s}^{-1}$; **d.** $k = 1.8 \times 10^{-14} \text{ molecules/cm}^3 \cdot \text{s}$ **75. a.** 25 kJ/mol; **b.** 12 s;

<i>c.</i> <i>T</i>	Interval	$54 - 2(\text{Intervals})$
21.0°C	16.3 s	21°C
27.8°C	13.0 s	28°C
30.0°C	12 s	30.°C

This rule of thumb gives excellent agreement to two significant figures.

Chapter 13

9. a. The rates of the forward and reverse reactions are equal. **b.** There is no net change in the composition. **11.** The equilibrium position depends on the initial concentrations of an experiment. Since there are an in-

finite number of initial conditions, then there are an infinite number of equilibrium positions. However, each one of these infinite equilibrium positions will always give the same value for the equilibrium constant. **13.** For the gas-phase reaction $aA + bB \rightleftharpoons cC + dD$,

the equilibrium constant expression is $K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$

and the reaction quotient has the same form $Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$.

The difference is that the expression for K uses equilibrium concentrations; that is, $[A]$, $[B]$, $[C]$, $[D]$ are all in equilibrium with each other. Any set of concentrations can be plugged into the reaction quotient expression. Typically, we plug in initial concentrations into the Q expression, then compare the value of Q to K to see how far we are from equilibrium. If $Q = K$, then the reaction is at equilibrium with these concentrations. If $Q \neq K$, then the reaction will have to shift either to products or to reactants to reach equilibrium. **15.** No, equilibrium is a dynamic process. Both the forward and reverse reactions are occurring at equilibrium, just at equal rates. Thus the forward and reverse reactions will distribute ^{14}C atoms between CO and CO_2 . **17.** 4 molecules H_2O , 2 molecules CO , 4 molecules H_2 , and 4 molecules CO_2 are present at equilibrium

$$\mathbf{19. a.} K = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]}; \quad \mathbf{b.} K = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}; \quad \mathbf{c.} K = \frac{[\text{SiCl}_4][\text{H}_2]^2}{[\text{SiH}_4][\text{Cl}_2]^2};$$

$$\mathbf{d.} K = \frac{[\text{PCl}_3]^2[\text{Br}_2]^3}{[\text{PBr}_3]^2[\text{Cl}_2]^3} \quad \mathbf{21. a.} 0.11; \quad \mathbf{b.} 77; \quad \mathbf{c.} 8.8; \quad \mathbf{d.} 1.7 \times 10^{-4}$$

$$\mathbf{23.} 6.9 \times 10^{-4} \quad \mathbf{25.} 1.7 \times 10^{-5} \quad \mathbf{27.} 6.3 \times 10^{-13} \quad \mathbf{29.} 1.5 \times 10^8$$

$$\mathbf{31. a.} K = \frac{1}{[\text{O}_2]^5}; K_p = \frac{1}{P_{\text{O}_2}^5}; \quad \mathbf{b.} K = [\text{N}_2\text{O}][\text{H}_2\text{O}]^2; K_p = P_{\text{N}_2\text{O}} \times P_{\text{H}_2\text{O}}^2;$$

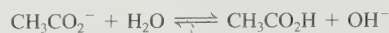
$$\mathbf{c.} K = \frac{1}{[\text{CO}_2]}; K_p = \frac{1}{P_{\text{CO}_2}}; \quad \mathbf{d.} K = \frac{[\text{SO}_2]^8}{[\text{O}_2]^8}; K_p = \frac{P_{\text{SO}_2}^8}{P_{\text{O}_2}^8}; \quad \mathbf{33.} 8.0 \times 10^9$$

35. a. $Q > K$, so reaction shifts left to reach equilibrium. **b.** $Q = K$, so reaction is at equilibrium. **c.** $Q < K$, so reaction shifts right to reach equilibrium. **37. a.** decrease; **b.** no change; **c.** no change; **d.** increase **39.** $0.096 M$ **41.** 3.4 **43.** 0.056 **45.** $[\text{SO}_3] = [\text{NO}] = 1.06 M$; $[\text{SO}_2] = [\text{NO}_2] = 0.54 M$ **47.** $7.8 \times 10^{-2} \text{ atm}$ **49.** $P_{\text{SO}_2} = 0.38 \text{ atm}$; $P_{\text{O}_2} = 0.44 \text{ atm}$; $P_{\text{SO}_3} = 0.12 \text{ atm}$ **51. a.** $[\text{NO}] = 0.032 M$; $[\text{Cl}_2] = 0.016 M$; $[\text{NOCl}] = 1.0 M$; **b.** $[\text{NO}] = [\text{NOCl}] = 1.0 M$; $[\text{Cl}_2] = 1.6 \times 10^{-5} M$; **c.** $[\text{NO}] = 8.0 \times 10^{-3} M$; $[\text{Cl}_2] = 1.0 M$; $[\text{NOCl}] = 2.0 M$ **53.** $[\text{CO}_2] = 0.39 M$; $[\text{CO}] = 8.6 \times 10^{-3} M$; $[\text{O}_2] = 4.3 \times 10^{-3} M$ **55.** 0.27 atm **57. a.** no effect; **b.** shifts left; **c.** shifts right **59. a.** right **b.** right; **c.** no effect; **d.** left; **e.** no effect **61. a.** left; **b.** right; **c.** left; **d.** no effect; **e.** no effect; **f.** right **63.** low temperatures **65.** 2.6×10^{81} **67.** $[\text{N}_2]_0 = 10.0 M$; $[\text{H}_2]_0 = 11.0 M$ **69. a.** 1.16 atm ; **b.** 0.10 atm ; **c.** 2.22 atm ; **d.** 91.4% **71.** $[\text{H}_2] = [\text{F}_2] = 0.0251 M$; $[\text{HF}] = 0.450 M$ **73.** Added OH^- reacts with H^+ to produce H_2O . As H^+ is removed, the reaction shifts right to produce more H^+ and CrO_4^{2-} . Since more CrO_4^{2-} is produced, then the solution turns yellow. **75.** $[\text{NOCl}] = 2.0 M$; $[\text{NO}] = 0.050 M$; $[\text{Cl}_2] = 0.025 M$ **77.** $2.1 \times 10^{-3} \text{ atm}$ **79.** $P_{\text{NO}_2} = 0.704 \text{ atm}$; $P_{\text{N}_2\text{O}_4} = 0.12 \text{ atm}$ **81.** 0.63

Chapter 14

17. a. Arrhenius acid: produce H^+ in water; **b.** Brønsted–Lowry acid: proton (H^+) donor; **c.** Lewis acid: electron-pair acceptor; the Lewis definition is most general. The Lewis definition can apply to all Arrhenius and Brønsted–Lowry acids; H^+ has an empty $1s$ orbital and forms bonds to all bases by accepting a pair of electrons from the base. In addition, the Lewis definition incorporates other reactions not typically considered acid–base reactions, e.g., $\text{BF}_3(\text{g}) + \text{NH}_3(\text{g}) \rightarrow \text{F}_3\text{B} \cdot \text{NH}_3(\text{s})$. NH_3 is something we usually consider a base, and it is in this reaction using the Lewis defini-

tion; NH_3 donates a pair of electrons to form the $\text{N} \rightarrow \text{B}$ bond. **19.** $[\text{H}^+] = [\text{OH}^-] = 1.0 \times 10^{-7} M$, $\text{pH} = 7.00$ **21.** An organic compound containing nitrogen with a lone pair of electrons will most likely produce a basic solution. The lone pair of electrons on nitrogen accepts the proton by forming a bond with the proton. **23. a.** stronger bond = stronger base; **b.** greater electronegativity = weaker base; **c.** more oxygen atoms = weaker base **25. a.** H_2O and CH_3CO_2^- ; **b.** CH_3CO_2^- , since the equilibrium favors acetic acid ($K_a < 1$); **c.** Acetate ion is a better base than water and produces basic solutions in water. When we put acetate ion into solution as the only major basic species, the reaction is



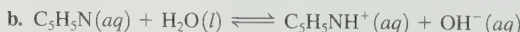
Now the competition is between CH_3CO_2^- and OH^- for the proton. Hydroxide ion is the strongest base possible in water. The above equilibrium favors acetate plus water resulting in a K_b value less than 1. Those species we specifically call weak bases ($10^{-14} < K_b < 1$) lie between H_2O and OH^- in base strength. Weak bases are stronger bases than water but are weaker bases than OH^- . **27.** When an acid dissociates, ions are produced. The conductivity of the solution is a measure of the number of ions. In addition, the colligative properties, as discussed in Chapter 11, depend on the number of particles present. Measurements of osmotic pressure, vapor pressure lowering, freezing-point depression, or boiling-point elevation will also allow us to determine the extent of ionization. **29. a.** $\text{HClO}_4(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_3\text{O}^+(\text{aq}) + \text{ClO}_4^-(\text{aq})$ or $\text{HClO}_4(\text{aq}) \rightarrow \text{H}^+(\text{aq}) + \text{ClO}_4^-(\text{aq})$; water is commonly omitted from K_a reactions. **b.** $\text{CH}_3\text{CH}_2\text{CO}_2\text{H}(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{CH}_3\text{CH}_2\text{CO}_2^-(\text{aq})$; **c.** $\text{NH}_4^+(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{NH}_3(\text{aq})$

31.

Acid	Base	Conjugate Base of Acid	Conjugate Acid of Base
a. HF	H_2O	F^-	H_3O^+
b. H_2SO_4	H_2O	HSO_4^-	H_3O^+
c. HSO_4^-	H_2O	SO_4^{2-}	H_3O^+

33. a. HClO_4 , strong acid; **b.** HOCl , weak acid; **c.** H_2SO_4 , strong acid; **d.** H_2SO_3 , weak acid **35.** $\text{HNO}_3 > \text{HOCl} > \text{NH}_4^+ > \text{H}_2\text{O}$ **37. a.** HCl ; **b.** HNO_2 ; **c.** HCN since it has a larger K_a value. **39. a.** $1.0 \times 10^{-7} M$; neutral; **b.** $1.5 \times 10^{-11} M$; acidic; **c.** $5.3 \times 10^{-4} M$; basic; **d.** $4.3 \times 10^{-15} M$; acidic **41. a.** endothermic; **b.** $[\text{H}^+] = [\text{OH}^-] = 2.34 \times 10^{-7} M$ **43. [39]** **a.** $\text{pH} = \text{pOH} = 7.00$; **b.** $\text{pH} = 3.17$; $\text{pOH} = 10.83$; **c.** $\text{pH} = 10.72$; $\text{pOH} = 3.28$; **d.** $\text{pH} = -0.36$; $\text{pOH} = 14.36$; **[40]** **a.** $\text{pH} = 14.56$; $\text{pOH} = -0.56$; **b.** $\text{pH} = 5.99$; $\text{pOH} = 8.01$; **c.** $\text{pH} = 11.34$; $\text{pOH} = 2.66$; **d.** $\text{pH} = \text{pOH} = 7.00$ **45. a.** $\text{pH} = 7.23$, $[\text{H}^+] = 1.7 \times 10^{-7} M$, $[\text{OH}^-] = 5.9 \times 10^{-8} M$, acidic **47. a.** H^+ , ClO_4^- , H_2O ; **b.** H^+ , NO_3^- , H_2O ; **0.602** **49.** $[\text{H}^+] = 0.088 M$, $[\text{OH}^-] = 1.1 \times 10^{-13} M$, $[\text{Cl}^-] = 0.013 M$, $[\text{NO}_3^-] = 0.075 M$ **51.** $3.2 \times 10^{-3} M$ **53. a.** HNO_2 and H_2O , 2.00 ; **b.** $\text{HC}_2\text{H}_3\text{O}_2$ and H_2O , 2.68 **55.** $5.0 \times 10^{-3} M$; 2.30 **57.** $[\text{H}^+] = [\text{F}^-] = 3.5 \times 10^{-3} M$, $[\text{OH}^-] = 2.9 \times 10^{-12} M$, $[\text{HF}] = 0.017 M$, 2.46 **59.** 1.96 **61. a.** 1.00 ; **b.** 1.30 **63. a.** 0.60% ; **b.** 1.9% ; **c.** 5.8% ; **d.** Dilution shifts equilibrium to the side with the greater number of particles (% dissociation increases). **e.** $[\text{H}^+]$ also depends on initial concentration of weak acid. **65.** 1.4×10^{-4} **67.** 3.5×10^{-4} **69.** $0.024 M$ **71. a.** $\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$



$$K_b = \frac{[\text{C}_5\text{H}_5\text{NH}^+][\text{OH}^-]}{[\text{C}_5\text{H}_5\text{N}]}$$

73. $\text{NH}_3 > \text{C}_5\text{H}_5\text{N} > \text{H}_2\text{O} > \text{NO}_3^-$ **75. a.** NH_3 ; **b.** NH_3 ; **c.** OH^- ; **d.** CH_3NH_2 **77. a.** 13.00 ; **b.** 7.00 ; **c.** 14.30 **79. a.** K^+ , OH^- , and H_2O , $0.015 M$, 12.18 ; **b.** Ba^{2+} , OH^- , and H_2O , $0.030 M$, 12.48 **81.** $3.2 \times 10^{-4} M$ **83.** NH_3 and H_2O , $1.6 \times 10^{-3} M$, 11.20

- 85.** $[\text{OH}^-] = 8.9 \times 10^{-13} \text{ M}$, $[\text{H}^+] = 1.1 \times 10^{-12} \text{ M}$, 11.96; **b.** $[\text{OH}^-] = 4.7 \times 10^{-5} \text{ M}$, $[\text{H}^+] = 2.1 \times 10^{-10} \text{ M}$, 9.68 **87.** 12.00 **89.** **a.** 1.3%; **b.** 4.2% **91.** 9.2×10^{-7}
- 93.** $\text{H}_2\text{SO}_3(\text{aq}) \rightleftharpoons \text{HSO}_3^-(\text{aq}) + \text{H}^+(\text{aq})$ K_{a1} reaction
 $\text{HSO}_3^-(\text{aq}) \rightleftharpoons \text{SO}_3^{2-}(\text{aq}) + \text{H}^+(\text{aq})$ K_{a2} reaction
- 95.** **a.** 1.62; **b.** 3.68 **97.** -0.30 **99.** $\text{HCl} > \text{NH}_4\text{Cl} > \text{KCl} > \text{KCN} > \text{KOH}$ **101.** OCl^- **103.** $[\text{HN}_3] = [\text{OH}^-] = 2.3 \times 10^{-6} \text{ M}$, $[\text{Na}^+] = 0.010 \text{ M}$, $[\text{N}_3^-] = 0.010 \text{ M}$, $[\text{H}^+] = 4.3 \times 10^{-9} \text{ M}$ **105.** **a.** 5.82; **b.** 10.95 **107.** NaF **109.** 3.08 **111.** **a.** neutral; **b.** basic; $\text{NO}_2^- + \text{H}_2\text{O} \rightleftharpoons \text{HNO}_2 + \text{OH}^-$; **c.** acidic; $\text{C}_5\text{H}_5\text{NH}^+ \rightleftharpoons \text{C}_5\text{H}_5\text{N} + \text{H}^+$; **d.** acidic since NH_4^+ is a stronger acid than NO_2^- is a base; $\text{NH}_4^+ \rightleftharpoons \text{NH}_3 + \text{H}^+$; $\text{NO}_2^- + \text{H}_2\text{O} \rightleftharpoons \text{HNO}_2 + \text{OH}^-$; **e.** basic; $\text{OCl}^- + \text{H}_2\text{O} \rightleftharpoons \text{HOCl} + \text{OH}^-$; **f.** basic since OCl^- is a stronger base than NH_4^+ is an acid; $\text{OCl}^- + \text{H}_2\text{O} \rightleftharpoons \text{HOCl} + \text{OH}^-$, $\text{NH}_4^+ \rightleftharpoons \text{NH}_3 + \text{H}^+$ **113.** **a.** $\text{HIO}_3 < \text{HBrO}_3$; as the electronegativity of the central atom increases, acid strength increases. **b.** $\text{HNO}_2 < \text{HNO}_3$; as the number of oxygen atoms attached to the central atom increases, acid strength increases. **c.** $\text{HOI} < \text{HOCl}$; same reasoning as in part a. **d.** $\text{H}_3\text{PO}_3 < \text{H}_3\text{PO}_4$; same reasoning as in part b. **115.** **a.** $\text{H}_2\text{O} < \text{H}_2\text{S} < \text{H}_2\text{Se}$; acid strength increases as bond energy decreases. **b.** $\text{CH}_3\text{CO}_2\text{H} < \text{FCH}_2\text{CO}_2\text{H} < \text{F}_2\text{CHCO}_2\text{H} < \text{F}_3\text{CCO}_2\text{H}$; as the electronegativity of the neighboring atoms increases, acid strength increases. **c.** $\text{NH}_4^+ < \text{HONH}_3^+$; same reasoning as in part b. **d.** $\text{NH}_4^+ < \text{PH}_4^+$; same reasoning as in part a. **117.** **a.** basic; $\text{CaO}(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{Ca}(\text{OH})_2(\text{aq})$; **b.** acidic; $\text{SO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{SO}_3(\text{aq})$; **c.** acidic; $\text{Cl}_2\text{O}(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow 2\text{HOCl}(\text{aq})$ **119.** **a.** $\text{B}(\text{OH})_3$, acid; H_2O , base; **b.** Ag^+ , acid; NH_3 , base; **c.** BF_3 , acid; F^- , base **121.** $\text{Al}(\text{OH})_3(\text{s}) + 3\text{H}^+(\text{aq}) \rightarrow \text{Al}^{3+}(\text{aq}) + 3\text{H}_2\text{O}(\text{l})$; $\text{Al}(\text{OH})_3(\text{s}) + \text{OH}^-(\text{aq}) \rightarrow \text{Al}(\text{OH})_4^-(\text{aq})$ **123.** Fe^{3+} ; because it is smaller with a greater positive charge, Fe^{3+} will be more strongly attracted to a lone pair of electrons from a Lewis base. **125.** 990 mL H_2O **127.** NH_4Cl **129.** 3.00 **131.** **a.** 2.62; **b.** 2.4%; **c.** 8.48 **133.** **a.** 1.66; **b.** Fe^{2+} ions will produce a less acidic solution (higher pH) due to the lower charge on Fe^{2+} as compared with Fe^{3+} . As the charge on a metal ion increases, acid strength of the hydrated ion increases. **135.** acidic; $\text{HSO}_4^- \rightleftharpoons \text{SO}_4^{2-} + \text{H}^+$; 1.54 **137.** **a.** $\text{Hb}(\text{O}_2)_4$ in lungs, HbH_4^{4+} in cells; **b.** Decreasing $[\text{CO}_2]$ will decrease $[\text{H}^+]$, favoring $\text{Hb}(\text{O}_2)_4$ formation. Breathing into a bag raises $[\text{CO}_2]$. **c.** NaHCO_3 lowers the acidity from accumulated CO_2 . **139.** **a.** H_2SO_3 ; **b.** HClO_3 ; **c.** H_3PO_3 ; NaOH and KOH are ionic compounds composed of either Na^+ or K^+ cations and OH^- anions. When soluble ionic compounds dissolve in water, they form the ions from which they are formed. The acids in this problem are all covalent compounds. When these acids dissolve in water, the covalent bond between oxygen and hydrogen breaks to form H^+ ions. **141.** 7.20 **143.** 7.4; when an acid is added to water, the pH cannot be basic. Must account for the autoionization of water. **145.** 0.022 **M** **147.** PO_4^{3-} , $K_{\text{b}} = 0.021$; HPO_4^{2-} , $K_{\text{b}} = 1.6 \times 10^{-7}$; H_2PO_4^- , $K_{\text{b}} = 1.3 \times 10^{-12}$; from the K_{b} values, PO_4^{3-} is the strongest base. **149.** 1.0×10^{-3}

Chapter 15

13. A common ion is an ion that appears in an equilibrium reaction but came from a source other than that reaction. Addition of a common ion (H^+ or NO_2^-) to the reaction $\text{HNO}_2 \rightleftharpoons \text{H}^+ + \text{NO}_2^-$ will drive the equilibrium to the left as predicted by Le Châtelier's principle. **15.** No, as long as there are both a weak acid and a weak base present, the solution will be buffered. If the concentrations are the same, the buffer will have the same capacity toward both added H^+ and OH^- . **17.** No, since there are three colored forms, there must be two proton transfer reactions. Thus there must be at least two acidic protons in the acid (orange) form of thymol blue. **19.** The two forms of an indicator are different colors. To see only one color, that form must be in tenfold excess or greater over the other. When the ratio of the two forms is less than 10, both colors are present. To go from $[\text{HIn}]/[\text{In}^-] = 10$ to $[\text{HIn}]/[\text{In}^-] = 0.1$ requires a change of 2 pH units as the indicator changes from the acid color to the base color. **21.** When strong acid or strong base is added to a sodium bicarbonate/sodium carbonate buffer mixture, the strong acid/base is neutralized. The reaction goes to completion resulting in the strong acid/base

being replaced with a weak acid/base. This results in a new buffer solution. The reactions are $\text{H}^+(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) \rightarrow \text{HCO}_3^-(\text{aq})$; $\text{OH}^-(\text{aq}) + \text{HCO}_3^-(\text{aq}) \rightarrow \text{CO}_3^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l})$ **23.** **a.** 2.96; **b.** 8.94; **c.** 7.00; **d.** 4.89 **25.** 1.1% vs. $1.3 \times 10^{-2}\%$ dissociated; the presence of $\text{C}_3\text{H}_5\text{O}_2^-$ in solution 23d greatly inhibits the dissociation of $\text{HC}_3\text{H}_5\text{O}_2$. This is called the *common ion effect*. **27.** **a.** 1.70; **b.** 5.49; **c.** 1.70; **d.** 4.71 **29.** **a.** 4.29; **b.** 12.30; **c.** 12.30; **d.** 5.07 **31.** solution d; solution d is a buffer solution that resists pH changes. **33.** 3.40 **35.** 3.48; 3.22 **37.** **a.** 5.14; **b.** 4.34; **c.** 4.74; **d.** 11.04; **e.** 10.74 **39.** **a.** 7.97; **b.** 8.73; both solutions have an initial pH = 8.77. The two solutions differ in their buffer capacity. Solution b with the larger concentrations has the greater capacity to resist pH change. **41.** 15 g **43.** **a.** 0.19; **b.** 0.59; **c.** 1.0; **d.** 1.9 **45.** HOCl ; there are many possibilities. One possibility is a solution with $[\text{HOCl}] = 1.0 \text{ M}$ and $[\text{NaOCl}] = 0.35 \text{ M}$. **47.** solution d **49.** **a.** 1.0 mol; **b.** 0.30 mol; **c.** 1.3 mol **51.** **a.** ~22 mL base added; **b.** buffer region is from ~1 mL to ~21 mL base added. The maximum buffering region would be from ~5 mL to ~17 mL of base added with the halfway point to equivalence (~11 mL) as the best buffer point. **c.** ~11 mL base added; **d.** 0 mL base added; **e.** ~22 mL base added (the stoichiometric point); **f.** any point after the stoichiometric point (volume base added > ~22 mL) **53.** **a.** 0.699; **b.** 0.854; **c.** 1.301; **d.** 7.00; **e.** 12.15 **55.** **a.** 2.72; **b.** 4.26; **c.** 4.74; **d.** 5.22; **e.** 8.79; **f.** 12.15

57. Volume (mL) pH

0.0	2.43
4.0	3.14
8.0	3.53
12.5	3.86
20.0	4.46
24.0	5.24
24.5	5.6
24.9	6.3
25.0	8.28
25.1	10.3
26.0	11.29
28.0	11.75
30.0	11.96

See *Solutions Guide* for pH plot.

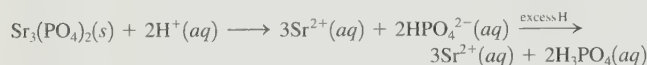
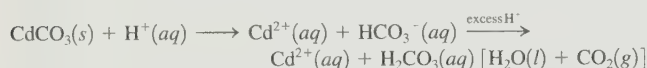
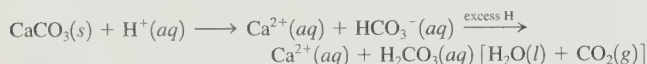
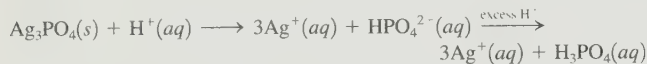
59. Volume (mL) pH

0.0	11.11
4.0	9.97
8.0	9.58
12.5	9.25
20.0	8.65
24.0	7.87
24.5	7.6
24.9	6.9
25.0	5.28
25.1	3.7
26.0	2.71
28.0	2.24
30.0	2.04

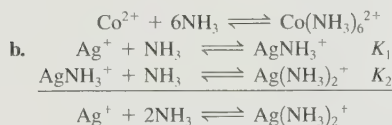
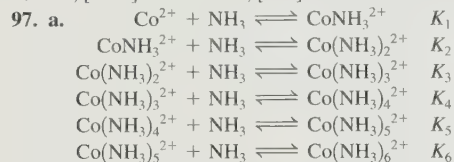
See *Solutions Guide* for pH plot.

- 61.** **a.** 4.19, 8.45; **b.** 10.74; 5.96; **c.** 0.89, 7.00 **63.** 1.74×10^{-8} **65.** **a.** yellow; **b.** 8.0; **c.** blue **67.** Phenol red is one possible indicator for the titration in Exercise 53. Phenolphthalein is one possible indicator for the titration in Exercise 55. **69.** Phenolphthalein is one possible indicator for Exercise 57. Bromocresol green is one possible indicator for Exercise 59. **71.** The pH is between 5 and 8. **73.** **a.** $\text{AgC}_2\text{H}_3\text{O}_2(\text{s}) \rightleftharpoons \text{Ag}^+(\text{aq}) + \text{C}_2\text{H}_3\text{O}_2^-(\text{aq})$; $K_{\text{sp}} = [\text{Ag}^+][\text{C}_2\text{H}_3\text{O}_2^-]$; **b.** $\text{Al}(\text{OH})_3(\text{s}) \rightleftharpoons \text{Al}^{3+}(\text{aq}) + 3\text{OH}^-(\text{aq})$; $K_{\text{sp}} = [\text{Al}^{3+}][\text{OH}^-]^3$; **c.** $\text{Ca}_3(\text{PO}_4)_2(\text{s}) \rightleftharpoons 3\text{Ca}^{2+}(\text{aq}) + 2\text{PO}_4^{3-}(\text{aq})$; $K_{\text{sp}} = [\text{Ca}^{2+}]^3[\text{PO}_4^{3-}]^2$ **75.** **a.** 2.3×10^{-9} ; **b.** 8.20×10^{-19} **77.** 3.92×10^{-5} **79.** **a.** $1.6 \times 10^{-5} \text{ mol/L}$; **b.** $9.3 \times$

10^{-5} mol/L; **c.** 6.5×10^{-7} mol/L **81.** 2.5×10^{-22} mol/L **83. a.** CaF_2 ; **b.** FePO_4 **85. a.** 4×10^{-17} mol/L; **b.** 4×10^{-11} mol/L; **c.** 4×10^{-29} mol/L **87.** 2.3×10^{-11} mol/L **89.** If the anion in the salt can act as a base in water, then the solubility of the salt will increase as the solution becomes more acidic. Added H^+ will react with the base, forming the conjugate acid. As the basic anion is removed, more of the salt will dissolve to replenish the basic anion. The salts with basic anions are Ag_3PO_4 , CaCO_3 , CdCO_3 , and $\text{Sr}_3(\text{PO}_4)_2$. Hg_2Cl_2 and PbI_2 do not have any pH dependence because Cl^- and I^- are terrible bases (the conjugate bases of strong acids).



91. yes; $Q = 1.9 \times 10^{-4} > K_{\text{sp}}$ **93.** $[\text{K}^+] = 0.160 \text{ M}$, $[\text{C}_2\text{O}_4^{2-}] = 3.3 \times 10^{-7} \text{ M}$, $[\text{Ba}^{2+}] = 0.0700 \text{ M}$, $[\text{Br}^-] = 0.300 \text{ M}$ **95.** $[\text{Ag}^+] > 5.6 \times 10^{-5} \text{ M}$



99. $\text{Hg}_2^{2+}(aq) + 2\text{I}^-(aq) \rightarrow \text{HgI}_2(s)$ (orange precipitate); $\text{HgI}_2(s) + 2\text{I}^-(aq) \rightarrow \text{HgI}_4^{2-}(aq)$ (soluble complex ion) **101.** $3.3 \times 10^{-32} \text{ M}$ **103. a.** $1.2 \times 10^{-8} \text{ mol/L}$; **b.** $1.5 \times 10^{-4} \text{ mol/L}$; **c.** The presence of NH_3 increases the solubility of AgI . Added NH_3 removes Ag^+ from solution by forming the complex ion $\text{Ag}(\text{NH}_3)_2^+$. As Ag^+ is removed, more AgI will dissolve to replenish the Ag^+ concentration. **105.** Test tube 1: added Cl^- reacts with Ag^+ to form the silver chloride precipitate. The net ionic equation is $\text{Ag}^+(aq) + \text{Cl}^-(aq) \rightarrow \text{AgCl}(s)$. Test tube 2: added NH_3 reacts with Ag^+ ions to form the soluble complex ion $\text{Ag}(\text{NH}_3)_2^+$. As this complex ion forms, Ag^+ is removed from solution, which causes $\text{AgCl}(s)$ to dissolve. When enough NH_3 is added, then all of the silver chloride precipitate will dissolve. The equation is $\text{AgCl}(s) + 2\text{NH}_3(aq) \rightarrow \text{Ag}(\text{NH}_3)_2^+(aq) + \text{Cl}^-(aq)$. Test tube 3: added H^+ reacts with the weak base NH_3 to form NH_4^+ . As NH_3 is removed, Ag^+ ions are released to solution, which can then react with Cl^- to reform $\text{AgCl}(s)$. The equations are $\text{Ag}(\text{NH}_3)_2^+(aq) + 2\text{H}^+(aq) \rightarrow \text{Ag}^+(aq) + 2\text{NH}_4^+(aq)$ and $\text{Ag}^+(aq) + \text{Cl}^-(aq) \rightarrow \text{AgCl}(s)$.

107. $\text{pOH} = \text{p}K_b + \log \frac{[\text{acid}]}{[\text{base}]}$ **109. a.** potassium fluoride + HCl ;

b. benzoic acid + NaOH ; **c.** acetic acid + sodium acetate; **d.** HOCl + NaOH ; **e.** ammonium chloride + NaOH **111. a.** 1.8×10^9 ; **b.** 5.6×10^4 ; **c.** 1.0×10^{14} **113.** 4.4 L **115.** $180. \text{ g/mol}$; 3.3×10^{-4} ; assume acetylsalicylic acid is a weak monoprotic acid. **117.** 0.210 M **119.** $2.7 \times 10^{-5} \text{ mol/L}$; the solubility of hydroxyapatite will increase as a solution gets more acidic, since both phosphate and hydroxide can react with H^+ . $6 \times 10^{-8} \text{ mol/L}$; the hydroxyapatite in the tooth enamel is converted to the less soluble fluorapatite by fluoride-treated water. The less soluble fluorapatite will then be more difficult to dissolve, making teeth less susceptible to decay. See Chemical Impact on "Chemistry of Teeth." **121. a.** $6.7 \times 10^{-6} \text{ mol/L}$; **b.** $1.2 \times 10^{-13} \text{ mol/L}$; **c.** $\text{Pb}(\text{OH})_2(s)$ will not

form since $Q < K_{\text{sp}}$ **123.** 49 mL **125.** 3.9 L **127. a.** 200.0 mL ; **b. i.** H_2A , H_2O ; **ii.** H_2A , HA^- , H_2O , Na^+ ; **iii.** HA^- , H_2O , Na^+ ; **iv.** HA^- , A^{2-} , H_2O , Na^+ ; **v.** A^{2-} , H_2O , Na^+ ; **vi.** A^{2-} , H_2O , Na^+ , OH^- ; **c.** $K_{\text{a}1} = 1 \times 10^{-4}$; $K_{\text{a}2} = 1 \times 10^{-8}$ **129. a.** $5.8 \times 10^{-4} \text{ mol/L}$; **b.** Greater; F^- is a weak base ($K_b = 1.4 \times 10^{-11}$), so some of the F^- is removed by reaction with water. As F^- is removed, more SrF_2 will dissolve; **c.** $3.5 \times 10^{-3} \text{ mol/L}$

Chapter 16

7. a. A spontaneous process occurs without any outside intervention. **b.** Entropy is a measure of disorder or randomness. **c.** The system is the portion of the universe in which we are interested. **d.** The surroundings are everything else in the universe besides the system. **9.** Living organisms need an external energy source to produce the necessary "ordering." **11.** The more widely something is dispersed, the greater the disorder and the greater the work needed to overcome the disorder. It would be more advantageous to prevent contamination of the environment rather than clean it up later. **13.** $w_{\text{max}} = \Delta G$; when ΔG is negative, the magnitude of ΔG is equal to the maximum possible useful work obtainable from the process (at constant T and P). When ΔG is positive, the magnitude of ΔG is equal to the minimum amount of work that must be expended to make the process spontaneous. Due to waste energy (heat) in any real process, the amount of useful work obtainable from a spontaneous process is always less than w_{max} , and for a nonspontaneous reaction, an amount of work greater than w_{max} must be applied to make the process spontaneous. **15. a, b, c** **17.** We draw all of the possible arrangements of the two particles in the three levels.

2 kJ	—	—	<u>X</u>	—	<u>X</u>	<u>XX</u>
1 kJ	—	<u>X</u>	—	<u>XX</u>	<u>X</u>	—
0 kJ	<u>XX</u>	<u>X</u>	<u>X</u>	—	—	—
Total $E =$	0 kJ	1 kJ	2 kJ	2 kJ	3 kJ	4 kJ

The most likely total energy is 2 kJ. **19. a.** H_2 at 100°C and 0.5 atm ; **b.** N_2 at STP; **c.** $\text{H}_2\text{O}(l)$ **21. a.** negative; **b.** positive **23.** $\Delta G < 0$ for **b, c, d** **25.** $89.3 \text{ J/K} \cdot \text{mol}$ **27. a.** yes ($\Delta G < 0$); **b.** 196 K **29. a.** negative; **b.** positive; **c.** negative; **d.** positive **31. a.** $C_{\text{graphite}}(s)$; **b.** $\text{C}_2\text{H}_5\text{OH}(g)$; **c.** $\text{CO}_2(g)$ **33. a.** negative, -186 J/K ; **b.** positive, 187 J/K ; **c.** hard to predict since $\Delta n = 0$; 138 J/K **35.** $262 \text{ J/K} \cdot \text{mol}$ **37. a.** ΔH and ΔS are both positive; **b.** S_{rhombic} **39. a.** ΔH and ΔS are both negative; **b.** low temperatures **41. a.** $\Delta H^\circ = -803 \text{ kJ}$, $\Delta S^\circ = -4 \text{ J/K}$, $\Delta G^\circ = -802 \text{ kJ}$; **b.** $\Delta H^\circ = 2802 \text{ kJ}$, $\Delta S^\circ = -262 \text{ J/K}$, $\Delta G^\circ = 2880 \text{ kJ}$; **c.** $\Delta H^\circ = -416 \text{ kJ}$, $\Delta S^\circ = -209 \text{ J/K}$, $\Delta G^\circ = -354 \text{ kJ}$; **d.** $\Delta H^\circ = -176 \text{ kJ}$, $\Delta S^\circ = -284 \text{ J/K}$, $\Delta G^\circ = -91 \text{ kJ}$ **43.** $\text{CH}_4(g) + \text{CO}_2(g) \rightarrow \text{CH}_3\text{CO}_2\text{H}(l)$, $\Delta H^\circ = -16 \text{ kJ}$, $\Delta S^\circ = -240 \text{ J/K}$, $\Delta G^\circ = 56 \text{ kJ}$; $\text{CH}_3\text{OH}(g) + \text{CO}(g) \rightarrow \text{CH}_3\text{CO}_2\text{H}(l)$, $\Delta H^\circ = -173 \text{ kJ}$, $\Delta S^\circ = -278 \text{ J/K}$, $\Delta G^\circ = -90 \text{ kJ}$; the second reaction is preferred. It should be run at temperatures below 622 K . **45.** $-300. \text{ kJ}$ **47.** -731 kJ/mol **49.** -4172 kJ **51.** -188 kJ **53. a.** shifts right; **b.** no shift since the reaction is at equilibrium; **c.** shifts left **55.** 8.72 ; 0.0789 **57. a.** 79.9 kJ/mol ; **b.** 81.1 kJ/mol **59.** -71 kJ/mol **61.** $\Delta H^\circ = 1.1 \times 10^5 \text{ J/mol}$; $\Delta S^\circ = 330 \text{ J/K} \cdot \text{mol}$; The major difference in the plot is the slope of the line. An endothermic process has a negative slope for the $\ln(K)$ versus $1/T$ plot, whereas an exothermic process has a positive slope. **63.** ΔS_{univ} **65.** The introduction of mistakes is an effect of entropy. The purpose of redundant information is to provide a control to check the "correctness" of the transmitted information. **67.** 370 K **69.** 60 **71. a.** $1.8 \times 10^4 \text{ J/mol}$; shifts left; **b.** 0 ; no shift since at equilibrium; **c.** $-1.1 \times 10^4 \text{ J/mol}$; shifts right; **d.** 0 ; no shift since at equilibrium; **e.** $2 \times 10^3 \text{ J/mol}$; shifts left **73. a.** 2.22×10^5 ; **b.** 94.3 **75.** ΔS is more favorable for reaction 2 than for reaction 1, resulting in $K_2 > K_1$. In reaction 1, seven particles in solution form one particle. In reaction 2, four particles form one, which

results in a smaller decrease in disorder than for reaction 1. **77.** $\Delta H^\circ = 286 \text{ kJ}$; $\Delta G^\circ = 326 \text{ kJ}$; $K = 7.22 \times 10^{-58}$; $P_{\text{O}_3} = 3.3 \times 10^{-41} \text{ atm}$; This partial pressure represents one molecule of ozone per $9.5 \times 10^{17} \text{ L}$ of air. Equilibrium is probably not maintained under the conditions because the concentration of ozone is not large enough to maintain equilibrium

79. a. Since $k_f = A \exp\left(\frac{-E_a}{RT}\right)$ and $k_r = A \exp\left(\frac{-(E_a - \Delta G^\circ)}{RT}\right)$, then $\frac{k_f}{k_r} = \exp\left(\frac{-E_a}{RT} + \frac{(E_a - \Delta G^\circ)}{RT}\right) = \exp\left(\frac{-\Delta G^\circ}{RT}\right)$. Since $K = \exp\left(\frac{-\Delta G^\circ}{RT}\right)$, then $K = \frac{k_f}{k_r}$. **b.** A catalyst increases the value of the rate constant (increases rate) by lowering the activation energy. For the equilibrium constant K to remain constant, both k_f and k_r must increase by the same factor. Therefore, a catalyst must increase the rate of both the forward and the reverse reactions. **81. a.** 0.333; **b.** $P_A = 1.50 \text{ atm}$; $P_B = 0.50 \text{ atm}$; **c.** $\Delta G = \Delta G^\circ + RT \ln(P_B/P_A) = 2722 \text{ J} - 2722 \text{ J} = 0$ **83.** at least 7.5 torr **85.** 16 g

Chapter 17

13. Oxidation: increase in oxidation number, loss of electrons; reduction: decrease in oxidation number, gain of electrons **15.** Reactions a, b, and c are oxidation–reduction reactions.

Oxidizing Agent	Reducing Agent	Substance Oxidized	Substance Reduced
a. H_2O	CH_4	$\text{CH}_4(\text{C})$	$\text{H}_2\text{O}(\text{H})$
b. AgNO_3	Cu	Cu	$\text{AgNO}_3(\text{Ag})$
c. HCl	Zn	Zn	$\text{HCl}(\text{H})$

17. In a galvanic cell a spontaneous reaction occurs, producing an electric current. In an electrolytic cell electricity is used to force a reaction to occur that is not spontaneous. **19. a.** cathode: where reduction occurs; **b.** anode: where oxidation occurs; **c.** oxidation half-reaction: e^- are products; **d.** reduction half-reaction: e^- are reactants **21.** As a battery discharges, $\mathcal{E}_{\text{cell}}$ decreases, eventually reaching zero. A charged battery is not at equilibrium. At equilibrium, $\mathcal{E}_{\text{cell}} = 0$ and $\Delta G = 0$. We get no work out of an equilibrium system. A battery is useful to us because it can do work as it approaches equilibrium. **23.** Both fuel cells and batteries are galvanic cells. However, fuel cells, unlike batteries, have the reactants continuously supplied and can produce a current indefinitely. **25.** See Figure 17.2 of the text for a typical galvanic cell. The anode compartment contains the oxidation half-reaction compounds/ions, and the cathode compartment contains the reduction half-reaction compounds/ions. The electrons flow from the anode to the cathode. For each of the following answers, all solutes are 1.0 M and all gases are at 1.0 atm. **a.** $7\text{H}_2\text{O}(\text{l}) + 2\text{Cr}^{3+}(\text{aq}) + 3\text{Cl}_2(\text{g}) \rightarrow \text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 6\text{Cl}^-(\text{aq}) + 14\text{H}^+(\text{aq})$; cathode: Pt electrode; Cl_2 bubbled into solution, Cl^- in solution; anode: Pt electrode; Cr^{3+} , H^+ , and $\text{Cr}_2\text{O}_7^{2-}$ in solution; **b.** $\text{Cu}^{2+}(\text{aq}) + \text{Mg}(\text{s}) \rightarrow \text{Cu}(\text{s}) + \text{Mg}^{2+}(\text{aq})$; cathode: Cu electrode; Cu^{2+} in solution; anode: Mg electrode; Mg^{2+} in solution **27. a.** 0.03 V; **b.** 2.71 V **29.** See Exercise 25 for a description of a galvanic cell. For each of the following answers, all solutes are 1.0 M and all gases are at 1.0 atm. In the salt bridge, cations flow to the cathode and anions flow to the anode. **a.** $\text{Cl}_2(\text{g}) + 2\text{Br}^-(\text{aq}) \rightarrow \text{Br}_2(\text{aq}) + 2\text{Cl}^-(\text{aq})$ $\mathcal{E}^\circ = 0.27 \text{ V}$; cathode: Pt electrode; $\text{Cl}_2(\text{g})$ bubbled in, Cl^- in solution; anode: Pt electrode; Br_2 and Br^- in solution; **b.** $3\text{H}_2\text{O}(\text{l}) + 5\text{IO}_4^-(\text{aq}) + 2\text{Mn}^{2+}(\text{aq}) \rightarrow 5\text{IO}_3^-(\text{aq}) + 2\text{MnO}_4^-(\text{aq}) + 6\text{H}^+(\text{aq})$ $\mathcal{E}^\circ = 0.09 \text{ V}$; cathode: Pt electrode; IO_4^- , IO_3^- , and H_2SO_4 (as a source of H^+) in solution; anode: Pt electrode; Mn^{2+} , MnO_4^- , and H_2SO_4 in solution **31.** 25a. $\text{Pt}|\text{Cr}^{3+}(1.0 \text{ M}), \text{H}^+(1.0 \text{ M}), \text{Cr}_2\text{O}_7^{2-}(1.0 \text{ M})||\text{Cl}_2(1.0 \text{ atm})|\text{Cl}^-(1.0 \text{ M})| \text{Pt}$; 25b. $\text{Mg}|\text{Mg}^{2+}(1.0 \text{ M})||\text{Cu}^{2+}(1.0 \text{ M})|\text{Cu}$; 29a. $\text{Pt}|\text{Br}_2(1.0 \text{ M}), \text{Br}^-(1.0 \text{ M})||\text{Cl}_2(1.0 \text{ atm})|\text{Cl}^-(1.0 \text{ M})| \text{Pt}$; 29b.

$\text{Pt}|\text{Mn}^{2+}(1.0 \text{ M}), \text{MnO}_4^-(1.0 \text{ M}), \text{H}^+(1.0 \text{ M})||\text{IO}_4^-(1.0 \text{ M}), \text{H}^+(1.0 \text{ M})|\text{IO}_3^-(1.0 \text{ M})| \text{Pt}$ **33. a.** $\text{Au}^{3+}(\text{aq}) + 3\text{Cu}^+(\text{aq}) \rightarrow 3\text{Cu}^{2+}(\text{aq}) + \text{Au}(\text{s})$ $\mathcal{E}^\circ = 1.34 \text{ V}$; **b.** $2\text{VO}_2^+(\text{aq}) + 4\text{H}^+(\text{aq}) + \text{Cd}(\text{s}) \rightarrow \text{Cd}^{2+}(\text{aq}) + 2\text{VO}^{2+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$ $\mathcal{E}^\circ = 1.40 \text{ V}$ **35. a.** $\mathcal{E}^\circ = 0.46 \text{ V}$, spontaneous; **b.** $\mathcal{E}^\circ = -0.53 \text{ V}$, not spontaneous **37.** $\mathcal{E}^\circ = 0.41 \text{ V}$; $\Delta G^\circ = -79 \text{ kJ}$ **39.** 33a. -388 kJ ; 33b. $-270. \text{ kJ}$ **41.** 1.21 V **43.** $\text{K}^+ < \text{H}_2\text{O} < \text{Cd}^{2+} < \text{I}_2 < \text{AuCl}_4^- < \text{IO}_3^-$ **45. a.** no; **b.** yes; **c.** yes; **d.** no **47. a.** $\text{Cr}_2\text{O}_7^{2-}$, O_2 , MnO_2 , IO_3^- ; **b.** PbSO_4 , Cd^{2+} , Fe^{2+} , Cr^{3+} , Zn^{2+} , H_2O **49.** $\text{ClO}^-(\text{aq}) + 2\text{NH}_3(\text{aq}) \rightarrow \text{Cl}^-(\text{aq}) + \text{N}_2\text{H}_4(\text{aq}) + \text{H}_2\text{O}(\text{l})$ $\mathcal{E}^\circ_{\text{cell}} = 1.00 \text{ V}$; Since $\mathcal{E}^\circ_{\text{cell}}$ is positive for this reaction, then at standard conditions ClO^- can spontaneously oxidize NH_3 to the somewhat toxic N_2H_4 . **51. a.** larger; **b.** smaller **53.** Electron flow is always from the anode to the cathode. For the cells with a nonzero cell potential, we will identify the cathode, which means the other compartment is the anode. **a.** 0; **b.** 0.018 V; compartment with $[\text{Ag}^+] = 2.0 \text{ M}$ is cathode; **c.** 0.059 V; compartment with $[\text{Ag}^+] = 1.0 \text{ M}$ is cathode; **d.** 0.26 V; compartment with $[\text{Ag}^+] = 1.0 \text{ M}$ is cathode; **e.** 0 **55.** yes **57.** 1.09 V **59. a.** 0.23 V; **b.** $1.2 \times 10^{-5} \text{ M}$ **61.** 0.16 V, copper is oxidized. **63.** [25] **a.** $\Delta G^\circ = -20 \text{ kJ}$; 1×10^3 ; **b.** $\Delta G^\circ = -523 \text{ kJ}$; 5.12×10^{91} ; [29] **a.** $\Delta G^\circ = -52 \text{ kJ}$; 1.4×10^6 ; **b.** $\Delta G^\circ = -90 \text{ kJ}$; 2×10^{15} **65. a.** no reaction; **b.** $\text{Cl}_2(\text{g}) + 2\text{I}^-(\text{aq}) \rightarrow \text{I}_2(\text{s}) + 2\text{Cl}^-(\text{aq})$ $\mathcal{E}^\circ_{\text{cell}} = 0.82 \text{ V}$, $\Delta G^\circ = -160 \text{ kJ}$; $K = 5.6 \times 10^{27}$; **c.** no reaction; **d.** $4\text{Fe}^{2+}(\text{aq}) + 4\text{H}^+(\text{aq}) + \text{O}_2(\text{g}) \rightarrow 4\text{Fe}^{3+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$ $\mathcal{E}^\circ_{\text{cell}} = 0.46 \text{ V}$; $\Delta G^\circ = -180 \text{ kJ}$; $K = 1.3 \times 10^{31}$; **67. a.** $\text{Au}^{3+}(\text{aq}) + 3\text{Ti}(\text{s}) \rightarrow \text{Au}(\text{s}) + 3\text{Ti}^+(\text{aq})$ $\mathcal{E}^\circ_{\text{cell}} = 1.84 \text{ V}$; **b.** $\Delta G^\circ = -533 \text{ kJ}$; $K = 2.52 \times 10^{93}$; **c.** 2.04 V **69.** 3.9×10^{-28} **71.** 1.6×10^{11} **73. a.** 30. hours; **b.** 33 s; **c.** 1.3 hours **75. a.** 16 g; **b.** 25 g; **c.** 71 g; **d.** 4.9 g **77. Sc** **79.** 9.12 L F_2 (anode), 29.2 g K (cathode) **81.** $7.44 \times 10^4 \text{ A}$ **83.** $1.14 \times 10^{-2} \text{ M}$ **85.** Au followed by Ag followed by Ni followed by Cd **87. a.** cathode: $\text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni}$; anode: $2\text{Br}^- \rightarrow \text{Br}_2 + 2\text{e}^-$; **b.** cathode: $\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$; anode: $2\text{F}^- \rightarrow \text{F}_2 + 2\text{e}^-$; **c.** cathode: $\text{Mn}^{2+} + 2\text{e}^- \rightarrow \text{Mn}$; anode: $2\text{I}^- \rightarrow \text{I}_2 + 2\text{e}^-$ **89. a.** 0.10 V, SCE is anode; **b.** 0.53 V, SCE is anode; **c.** 0.02 V, SCE is cathode; **d.** 1.90 V, SCE is cathode; **e.** 0.47 V, SCE is cathode **91. a.** decrease; **b.** increase; **c.** decrease; **d.** decrease; **e.** same **93. a.** $\Delta G^\circ = -582 \text{ kJ}$; $K = 3.45 \times 10^{102}$; $\Delta G^\circ = 1.01 \text{ V}$; **b.** -0.65 V ; **95.** The concentrations were such that $\text{Cr}_2\text{O}_7^{2-}$ oxidized Cl^- to form pungent fumes of $\text{Cl}_2(\text{g})$. **97.** The claim is impossible. The strongest oxidizing agent and reducing agent when combined only give $\mathcal{E}^\circ$ of about 6 V. **99.** $w_{\text{max}} = -13,200 \text{ kJ}$; the work done can be no larger than the free energy change. If the process were reversible all of the free energy released would go into work, but this does not occur in any real process. Fuel cells are more efficient in converting chemical energy to electrical energy; they are also less massive. Major disadvantage: They are expensive. **101.** 0.98 V **103.** +3 **105.** $\mathcal{E}^\circ = \frac{T\Delta S^\circ}{nF} - \frac{\Delta H^\circ}{nF}$; if we graph $\mathcal{E}^\circ$ vs. T , we should get a straight line ($y = mx + b$). The slope of the line is equal to $\Delta S^\circ/nF$ and the y-intercept is equal to $-\Delta H^\circ/nF$. $\mathcal{E}^\circ$ will have little temperature dependence for cell reactions with ΔS° close to zero. **107.** 9.8×10^{-6} **109.** 2.39×10^{-7} **111. a.** $\pm 0.02 \text{ pH units}$; $\pm 6 \times 10^{-6} \text{ M H}^+$; **b.** $\pm 0.001 \text{ V}$ **113. a.** 0.16 V; **b.** 8.6 mol

Chapter 18

1. Fission: Splitting of a heavy nucleus into two (or more) lighter nuclei.

Fusion: Combining two light nuclei to form a heavier nucleus.

The maximum binding energy per nucleon occurs at Fe. Nuclei smaller than Fe become more stable by fusing to form heavier nuclei closer to Fe. Nuclei larger than Fe form more stable nuclei by splitting to form lighter nuclei closer to Fe. **3.** Assume ^{14}C level is constant or can be determined at the time the object died. Constant ^{14}C level is a poor assumption and accounting for variation is complicated. Also, some of the material must be destroyed. **5.** No, coal-fired power plants also pose risks. A partial list of risks:

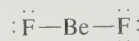
Coal	Nuclear
Air pollution	Radiation exposure to workers
Coal mine accidents	Disposal of wastes
Health risks to miners (black lung disease)	Meltdown
	Terrorists
	Public fear

7. For fusion a collision of sufficient energy must occur between two positively charged particles to initiate the reaction. This requires high temperatures. In fission, an electrically neutral neutron collides with the positively charged nucleus. This has a much lower activation energy. **9. a.** $^{51}_{24}\text{Cr} \rightarrow ^0_{-1}\text{e} + ^{51}_{23}\text{V}$; **b.** $^{131}_{53}\text{I} \rightarrow ^0_{-1}\text{e} + ^{131}_{54}\text{Xe}$ **11. a.** $^{68}_{31}\text{Ga} + ^0_{-1}\text{e} \rightarrow ^{68}_{30}\text{Zn}$; **b.** $^{62}_{29}\text{Cu} \rightarrow ^0_{-1}\text{e} + ^{62}_{28}\text{Ni}$; **c.** $^{212}_{87}\text{Fr} \rightarrow ^4_2\text{He} + ^{208}_{85}\text{At}$; **d.** $^{129}_{51}\text{Sb} \rightarrow ^0_{-1}\text{e} + ^{129}_{52}\text{Te}$ **13.** 10 α particles; 5 β particles **15.** $^{56}_{26}\text{Fe}$ has too many protons. It will undergo positron production, electron capture, and/or alpha-particle production. ^{59}Fe has too many neutrons and will undergo beta-particle production. (See Table 18.2 of the text.) **17. a.** $^{249}_{98}\text{Cf} + ^{18}_8\text{O} \rightarrow ^{263}_{106}\text{Sg} + 4^1_0\text{n}$; **b.** $^{259}_{104}\text{Rf}$ **19.** 690 hours **21.** ^{81}Kr is most stable since it has the longest half-life. ^{73}Kr is "hottest" since it decays very rapidly due to its very short half-life. ^{73}Kr , 81s; ^{74}Kr , 34.5 min; ^{76}Kr , 44.4 h; ^{81}Kr , 6.3×10^5 yr **23.** 6.22 mg ^{32}P remains **25.** 0.247 **27.** 2.3 counts per minute per gram of C. No; for a 10.-mg C sample, it would take roughly 40 min to see a single disintegration. This is too long to wait, and the background radiation would probably be much greater than the ^{14}C activity. Thus ^{14}C dating is not practical for very small samples. **29.** 3.8×10^9 yr **31.** 4.3×10^6 kg/s **33.** ^{232}Pu , -1.715×10^{14} J/mol; ^{231}Pa , -1.714×10^{14} J/mol **35.** ^{12}C : 1.23×10^{-12} J/nucleon; ^{235}U : 1.2155×10^{-12} J/nucleon; since ^{56}Fe is the most stable known nucleus, then the binding energy per nucleon for ^{56}Fe would be larger than that of ^{12}C or ^{235}U . (See Fig. 18.9 of the text.) **37.** -2.0×10^{10} J/g of hydrogen nuclei **39.** The Geiger-Müller tube has a certain response time. After the gas in the tube ionizes to produce a "count," some time must elapse for the gas to return to an electrically neutral state. The response of the tube levels off because at high activities radioactive particles are entering the tube faster than the tube can respond to them. **41.** All evolved $\text{O}_2(\text{g})$ comes from water. **43.** Strontium. Xe is chemically unreactive and not readily incorporated into the body. Sr can be easily oxidized to Sr^{2+} . Strontium is in the same family as calcium and could be absorbed and concentrated in the body in a fashion similar to Ca^{2+} . The chemical properties determine where radioactive material may be concentrated in the body or how easily it may be excreted. **45. a.** unstable; beta production; **b.** stable; **c.** unstable; positron production or electron capture; **d.** unstable, positron production, electron capture, or alpha production. **47.** 1975 **49.** 900 g ^{235}U **51.** Assuming that (1) the radionuclide is long lived enough that no significant decay occurs during the time of the experiment, and (2) the total activity is uniformly distributed only in the rat's blood; $V = 10.$ mL. **53. a.** ^{12}C ; **b.** ^{13}N , ^{13}C , ^{14}N , ^{15}O , and ^{15}N ; **c.** -5.950×10^{11} J/mol ^1H **55.** 4.3×10^{-29}

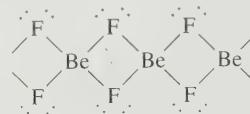
Chapter 19

1. The gravity of the earth cannot keep H_2 in the atmosphere. **3.** Ionic, covalent, and metallic (or interstitial). The ionic and covalent hydrides are true compounds that differ in the type of bonding. The interstitial hydrides are more like solid solutions of hydrogen and a transition metal and have variable content. **5.** Hydrogen forms many compounds in which its oxidation state is +1. On the other hand, hydrogen forms diatomic H_2 molecules and is a nonmetal, while the Group 1A elements are metals. Hydrogen forms the hydride anion H^- ; the Group 1A metals do not form stable anions. **7.** They must be produced in the absence of materials (H_2O , O_2) that are capable of oxidizing them. **9.** The planes of carbon atoms slide easily. Graphite is not volatile so the lubricant will not be lost when used in a high vacuum environment. **11.** p-type semiconductor **13. a.** $\Delta H^\circ = 207$ kJ, $\Delta S^\circ = 216$ J/K; **b.** $T > 958$ K **15. a.** lithium oxide; **b.** potassium superoxide; **c.** sodium peroxide **17. a.** $\text{Li}_2\text{O}(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow 2\text{LiOH}(\text{aq})$; **b.** $\text{Na}_2\text{O}_2(\text{s}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{NaOH}(\text{aq}) + \text{H}_2\text{O}_2(\text{aq})$; **c.** $\text{LiH}(\text{s}) + \text{H}_2\text{O}(\text{l})$

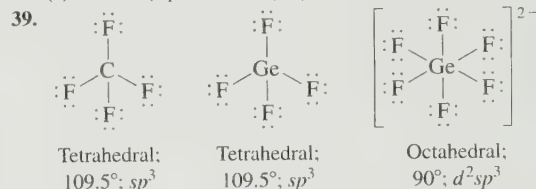
$\rightarrow \text{H}_2(\text{g}) + \text{LiOH}(\text{aq})$; **d.** $2\text{KO}_2(\text{s}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{KOH}(\text{aq}) + \text{O}_2(\text{g}) + \text{H}_2\text{O}_2(\text{aq})$ **19.** $2\text{Li}(\text{s}) + 2\text{C}_2\text{H}_2(\text{g}) \rightarrow 2\text{LiC}_2\text{H}(\text{s}) + \text{H}_2(\text{g})$; oxidation-reduction **21. a.** magnesium carbonate; **b.** barium sulfate; **c.** strontium hydroxide **23.** $\text{CaCO}_3(\text{s}) + \text{H}_2\text{SO}_4(\text{aq}) \rightarrow \text{CaSO}_4(\text{aq}) + \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g})$ **25.** In the gas phase, linear molecules would exist:



In the solid state, BeF_2 has the following extended structure:



27. $2 \times 10^{-2} M$ **29.** 3.84×10^6 g Ba **31. a.** AlN ; **b.** GaF_3 ; **c.** Ga_2S_3 **33.** $\text{B}_2\text{H}_6(\text{g}) + 3\text{O}_2(\text{g}) \rightarrow 2\text{B}(\text{OH})_3(\text{s})$ **35.** $\text{In}_2\text{O}_3(\text{s}) + 6\text{H}^+(\text{aq}) \rightarrow 2\text{In}^{3+}(\text{aq}) + 3\text{H}_2\text{O}(\text{l})$; $\text{In}_2\text{O}_3(\text{s}) + \text{OH}^-(\text{aq}) \rightarrow \text{no reaction}$; $\text{Ga}_2\text{O}_3(\text{s}) + 6\text{H}^+(\text{aq}) \rightarrow 2\text{Ga}^{3+}(\text{aq}) + 3\text{H}_2\text{O}(\text{l})$; $\text{Ga}_2\text{O}_3(\text{s}) + 2\text{OH}^-(\text{aq}) + 3\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{Ga}(\text{OH})_4^-(\text{aq})$ **37.** $2\text{Ga}(\text{s}) + 3\text{F}_2(\text{g}) \rightarrow 2\text{GaF}_3(\text{s})$; $4\text{Ga}(\text{s}) + 3\text{O}_2(\text{g}) \rightarrow 2\text{Ga}_2\text{O}_3(\text{s})$; $16\text{Ga}(\text{s}) + 3\text{S}_8(\text{s}) \rightarrow 8\text{Ga}_2\text{S}_3(\text{s})$; $2\text{Ga}(\text{s}) + \text{N}_2(\text{g}) \rightarrow 2\text{GaN}(\text{s})$; $2\text{Ga}(\text{s}) + 6\text{HCl}(\text{aq}) \rightarrow 2\text{GaCl}_3(\text{aq}) + 3\text{H}_2(\text{g})$



To form CF_6^{2-} , carbon would have to expand its octet of electrons. Carbon compounds do not expand their octet because of the small atomic size of carbon and because there are no low energy d orbitals on carbon to accommodate the extra electrons. **41. a.** $\text{SiO}_2(\text{s}) + 2\text{C}(\text{s}) \rightarrow \text{Si}(\text{s}) + 2\text{CO}(\text{g})$; **b.** $\text{SiCl}_4(\text{l}) + 2\text{Mg}(\text{s}) \rightarrow \text{Si}(\text{s}) + 2\text{MgCl}_2(\text{s})$; **c.** $\text{Na}_2\text{SiF}_6(\text{s}) + 4\text{Na}(\text{s}) \rightarrow \text{Si}(\text{s}) + 6\text{NaF}(\text{s})$ **43.** Lead is very toxic. As the temperature of the water increases, the solubility of Pb will increase. Drinking hot tap water from pipes containing lead solder could result in higher Pb concentrations in the body. **45.** $\text{C}_6\text{H}_{12}\text{O}_6(\text{aq}) \rightarrow 2\text{C}_2\text{H}_5\text{OH}(\text{aq}) + 2\text{CO}_2(\text{g})$ **47.** The π electrons are free to move in graphite, thus giving it a greater conductivity (lower resistance). The electrons have the greatest mobility within the sheets of carbon atoms. Electrons in diamond are not mobile (high resistance). The structure of diamond is uniform in all directions; thus there is no directional dependence of the resistivity. **49.** $-390.$ kJ; 30.0°C **51.** Strontium and calcium are both alkaline earth metals, so both have similar chemical properties. Since milk is a good source of calcium, strontium could replace some calcium in milk without much difficulty. **53.** The inert-pair effect refers to the difficulty of removing the pair of valence s electrons from some of the elements in the fifth and sixth periods of the periodic table. As a result, multiple oxidation states are exhibited for the heavier elements of Groups 3A (and 4A). In^+ , In^{3+} , Tl^+ , and Tl^{3+} oxidation states are all important to the chemistry of In and Tl. **55.** 3.08 **57.** If the compound contained Ga(II) it would be paramagnetic and if the compound contained Ga(I) and Ga(III), it would be diamagnetic. Paramagnetic compounds have an apparent greater mass in a magnetic field. **59.** 59 atm in the gas phase; 2.8 mol CO_2/L in the wine **61.** $\text{Pb}(\text{NO}_3)_2(\text{aq}) + \text{H}_3\text{AsO}_4(\text{aq}) \rightarrow \text{PbHAsO}_4(\text{s}) + 2\text{HNO}_3(\text{aq})$ **63.** $2.0 \times 10^{-37} M$ **65.** Carbon is much smaller than Si and cannot form a fifth bond in the transition state.

Chapter 20

1. a. This reaction is exothermic so an increase in temperature will decrease the value of K (see Table 13.3). This lowers the amount of $\text{NH}_3(\text{g})$ produced at equilibrium. The temperature increase, therefore, must be for

kinetic reasons. As temperature increases, the reaction reaches equilibrium much faster. At low temperatures, this reaction is too slow to be of any use.

b. As $\text{NH}_3(g)$ is removed, the reaction shifts right to produce more $\text{NH}_3(g)$.

c. A catalyst has no effect on the equilibrium position. The purpose of a catalyst is to speed up a reaction so it reaches equilibrium more quickly.

d. When the pressure of reactants and products is high, the reaction shifts to the side that has fewer gas molecules. Since the product side contains 2 molecules of gas as compared to 4 molecules of gas on the reactant side, then the reaction shifts to the right to the products at high pressures of reactants and products.

3. Pollutants provide nitrogen and phosphorus nutrients, causing the algae to grow, which consumes oxygen, causing fish to die.

5. Plastic sulfur has long S_n chains that break down into S_8 rings.

7. Fluorine is the most electronegative element; the F_2 bond is very weak.

9. Helium, which does not combine with other elements, has a low mass and easily escaped the earth's gravitational pull as the planet was formed.

11. Nitrogen's small size does not provide room for all four oxygen atoms, making NO_4^{3-} unstable. Phosphorus is larger so PO_4^{3-} is more stable. To form NO_3^- , a pi bond must form. Phosphorus doesn't form strong pi bonds as readily as nitrogen.

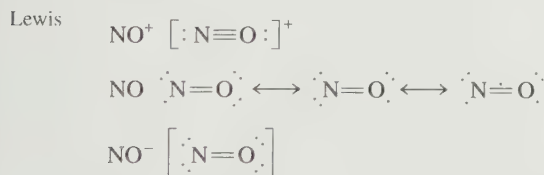
13. a. $\text{NH}_4\text{NO}_3(s) \xrightarrow{\text{Heat}} \text{N}_2\text{O}(g) + 2\text{H}_2\text{O}(g)$;
b. $2\text{N}_2\text{O}_5(g) \rightarrow 4\text{NO}_2(g) + \text{O}_2(g)$; **c.** $2\text{K}_3\text{P}(s) + 6\text{H}_2\text{O}(l) \rightarrow 2\text{PH}_3(g) + 6\text{KOH}(aq)$; **d.** $\text{PBr}_3(l) + 3\text{H}_2\text{O}(l) \rightarrow \text{H}_3\text{PO}_3(aq) + 3\text{HBr}(aq)$;
e. $2\text{NH}_3(aq) + \text{NaOCl}(aq) \rightarrow \text{N}_2\text{H}_4(aq) + \text{NaCl}(aq) + \text{H}_2\text{O}(l)$

15. $\text{CaF}_2 \cdot 3\text{Ca}_3(\text{PO}_4)_2(s) + 10\text{H}_2\text{SO}_4(aq) + 20\text{H}_2\text{O}(l) \rightarrow 6\text{H}_3\text{PO}_4(aq) + 2\text{HF}(aq) + 10\text{CaSO}_4 \cdot 2\text{H}_2\text{O}(s)$

17. 2.08 mol **19.** $\text{N}_2\text{H}_4(l) + \text{O}_2(g) \rightarrow \text{N}_2(g) + 2\text{H}_2\text{O}(g)$; $\Delta H = -590. \text{ kJ}$

21. $\frac{1}{2}\text{N}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{NO}(g)$ $\Delta G^\circ = \Delta G^\circ_{\text{f,NO}}$; NO (and some other oxides of nitrogen) have weaker bonds as compared with the triple bond of N_2 and the double bond of O_2 . Because of this, NO (and some other oxides of nitrogen) has a higher (positive) standard free energy of formation as compared to the relatively stable N_2 and O_2 molecules.

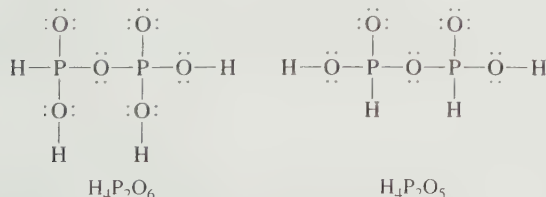
		Bond order	# unpaired e^-
M.O.	NO	2.5	1
	NO^+	3	0
	NO^-	2	2



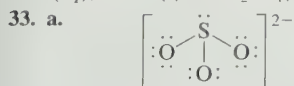
Lewis structures are not adequate for NO and NO^- . The M.O. model gives correct results for all three species. For NO, Lewis structures fail for odd-electron species. For NO^- , Lewis structures fail to predict that NO^- is paramagnetic.

25. a. $\text{H}_3\text{PO}_4 > \text{H}_3\text{PO}_3$; **b.** $\text{H}_3\text{PO}_4 > \text{H}_2\text{PO}_4^- > \text{HPO}_4^{2-}$

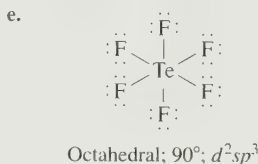
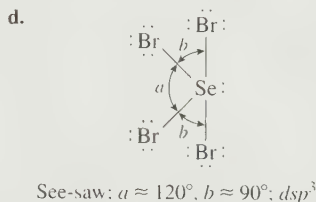
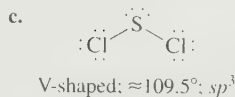
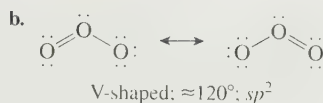
27. The acidic protons are attached to oxygen.



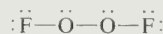
29. 821 nm **31. a.** $2\text{SO}_2(g) + \text{O}_2(g) \rightarrow 2\text{SO}_3(g)$; **b.** $\text{SO}_3(g) + \text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{SO}_4(aq)$; **c.** $2\text{Na}_2\text{S}_2\text{O}_3(aq) + \text{I}_2(aq) \rightarrow \text{Na}_2\text{S}_4\text{O}_6(aq) + 2\text{NaI}(aq)$; **d.** $\text{Cu}(s) + 2\text{H}_2\text{SO}_4(aq) \rightarrow \text{CuSO}_4(aq) + 2\text{H}_2\text{O}(l) + \text{SO}_2(aq)$



Trigonal pyramid; $\approx 109.5^\circ$; sp^3



35. From the following Lewis structure, each oxygen atom has a tetrahedral arrangement of electron pairs. Therefore, bond angles $\approx 109.5^\circ$, and each O is sp^3 hybridized.



Formal charge: 0 0 0 0

Oxidation state: -1 +1 +1 -1

Oxidation states are more useful. We are forced to assign +1 as the oxidation state for oxygen. Oxygen is very electronegative, and +1 is not a stable oxidation state for this element.

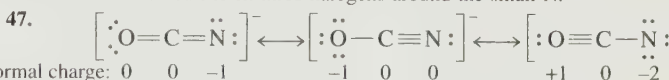
37. a. $\text{BaCl}_2(s) + \text{H}_2\text{SO}_4(aq) \rightarrow \text{BaSO}_4(s) + 2\text{HCl}(g)$; **b.** $\text{BrF}(s) + \text{H}_2\text{O}(l) \rightarrow \text{HF}(aq) + \text{HOBr}(aq)$; **c.** $\text{SiO}_2(s) + 4\text{HF}(aq) \rightarrow \text{SiF}_4(g) + 2\text{H}_2\text{O}(l)$

39. ClO^- can oxidize NH_3 to the somewhat toxic N_2H_4 .

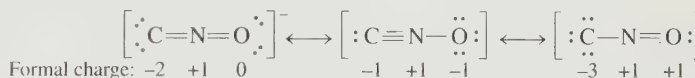
41. a. IO_4^- ; **b.** IO_3^- ; **c.** IF_2^- ; **d.** IF_4^- ; **e.** IF_6^-

43. XeF_2 can react with oxygen to produce explosive xenon oxides and oxyfluorides.

45. As the halogen atoms get larger, it becomes more difficult to fit three halogens around the small N.



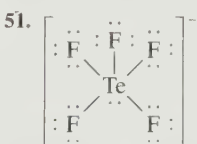
Formal charge: 0 0 -1 -1 0 0 +1 0 -2



Formal charge: -2 +1 0 -1 +1 -1 -3 +1 +1

All the resonance structures for fulminate involve greater formal charges than in cyanate, making fulminate more reactive (less stable).

49. 32 kg bacterial tissue

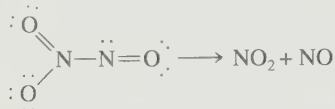


The lone pair of electrons around Te exerts a stronger repulsion than the bonding pairs, pushing the four square planar F's away from the lone pair.

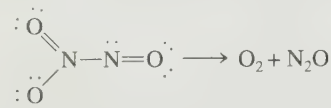
53. Release of Sr is probably more harmful. Xe is chemically unreactive. Strontium is in the same family as calcium and could be absorbed and concentrated in the body in a fashion similar to Ca. This puts the radioactive Sr in the bones; red blood cells are produced in bone marrow. Xe would not be readily incorporated in the body. The chemical properties determine

where a radioactive material may be concentrated in the body or how easily it may be excreted. The length of time of exposure and the route of exposure to radiation significantly affect the health hazard.

55. For the reaction



the activation energy must in some way involve the breaking of a nitrogen–nitrogen single bond. For the reaction

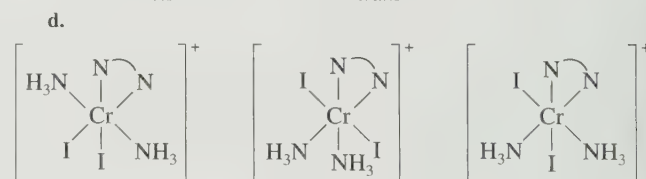
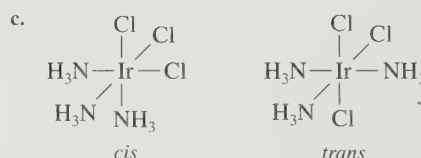
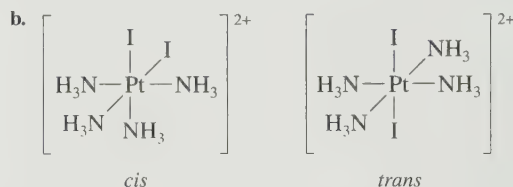
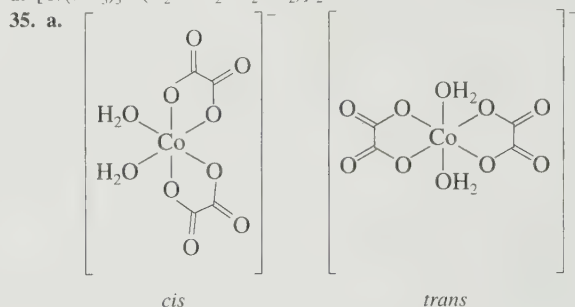


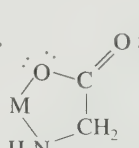
at some point nitrogen–oxygen bonds must be broken. N–N single bonds (160 kJ/mol) are weaker than N–O single bonds (201 kJ/mol). In addition, resonance structures indicate that there is more double-bond character in the N–O bonds than in the N–N bond. Thus NO_2 and NO are preferred by kinetics because of the lower activation energy. 57. a. NO ; b. NO_2 ; c. $k_{\text{cat}}/k_{\text{un}} = 2.3$; d. $\text{ClO(g)} + \text{O(g)} \rightarrow \text{O}_2\text{(g)} + \text{Cl(g)}$; $\text{O}_3\text{(g)} + \text{O(g)} \rightarrow 2\text{O}_2\text{(g)}$; e. The Cl-catalyzed reaction is roughly 52 times faster (more efficient) than the NO-catalyzed reaction.

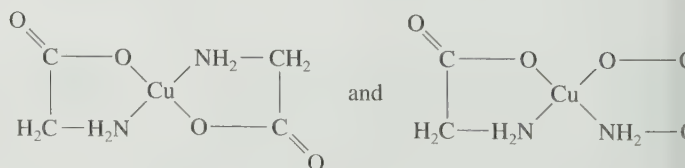
Chapter 21

5. a. ligand: species that donates a pair of electrons to form a covalent bond to a metal ion (a Lewis base); b. chelate: ligand that can form more than one bond; c. bidentate: ligand that forms two bonds; d. complex ion: metal ion plus ligands 7. a. isomers: species with the same formulas but different properties (see text for examples of the following types of isomers); b. structural isomers: isomers that have one or more bonds that are different; c. stereoisomers: isomers that contain the same bonds but differ in how the atoms are arranged in space; d. coordination isomers: structural isomers that differ in the atoms that make up the complex ion; e. linkage isomers: structural isomers that differ in how one or more ligands are attached to the transition metal; f. geometrical isomers: (*cis-trans* isomerism) stereoisomers that differ in the positions of atoms with respect to a rigid ring, bond, or each other; g. optical isomers: stereoisomers that are nonsuperimposable mirror images of each other; that is, they are different in the same way that our left and right hands are different. 9. Cu^{2+} is d^9 ; Cu^+ is d^{10} . Color results from electron transfer between split d orbitals. This cannot occur for the filled d orbitals in Cu^+ . Cd^{2+} , like Cu^+ , is also d^{10} . We would not expect $\text{Cd}(\text{NH}_3)_4\text{Cl}_2$ to be colored due to the filled d orbitals of Cd^{2+} . 11. The d -orbital splitting in tetrahedral complexes is less than one-half the d -orbital splitting in octahedral complexes. There are no known ligands powerful enough to produce the strong-field case; hence all tetrahedral complexes are weak field or high spin. 13. A soluble complex ion forms: $\text{Fe}_2\text{O}_3\text{(s)} + 6\text{H}_2\text{C}_2\text{O}_4\text{(aq)} \rightarrow 2\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}\text{(aq)} + 3\text{H}_2\text{O(l)} + 6\text{H}^+\text{(aq)}$ 15. There is a steady decrease in the atomic radii of the lanthanide elements, going from left to right. As a result, the properties of the $4d$ and $5d$ elements in each group are very similar because of the similar sizes of atoms and ions. 17. Advantages: low energy cost, less air pollution; disadvantage: chemicals used are expensive 19. a. Ni: $[\text{Ar}]4s^23d^8$; b. Cd: $[\text{Kr}]5s^24d^{10}$; c. Zr: $[\text{Kr}]5s^24d^2$; d. Os: $[\text{Xe}]6s^24f^{14}5d^6$ 21. a. Ti: $[\text{Ar}]4s^23d^2$; Ti^{2+} : $[\text{Ar}]3d^2$; Ti^{4+} : $[\text{Ne}]3s^23p^6$ or $[\text{Ar}]$; b. Re: $[\text{Xe}]6s^24f^{14}5d^5$; Re^{2+} : $[\text{Xe}]4f^{14}5d^5$; Re^{3+} : $[\text{Xe}]4f^{14}5d^4$; c. Ir: $[\text{Xe}]6s^24f^{14}5d^7$; Ir^{2+} : $[\text{Xe}]4f^{14}5d^7$; Ir^{3+} : $[\text{Xe}]4f^{14}5d^6$ 23. If rain is imminent, the large amount of water vapor in the air would cause the reaction to shift to the right. The indicator would take on the color of the pink $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$. 25. Test tube 1: added Cl^- reacts with Ag^+ to form the silver chloride precipitate. The net ionic equation is $\text{Ag}^+\text{(aq)} + \text{Cl}^-\text{(aq)} \rightarrow \text{AgCl(s)}$. Test tube 2: added NH_3 reacts with Ag^+ ions to form the soluble complex ion $\text{Ag}(\text{NH}_3)_2^+$. As this complex ion forms, Ag^+ is removed from

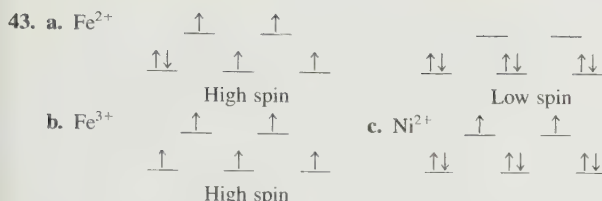
the solution, which causes the AgCl(s) to dissolve. When enough NH_3 is added, then all of the silver chloride precipitate will dissolve. The equation is $\text{AgCl(s)} + 2\text{NH}_3\text{(aq)} \rightarrow \text{Ag}(\text{NH}_3)_2^+\text{(aq)} + \text{Cl}^-\text{(aq)}$. Test tube 3: added H^+ reacts with the weak base NH_3 to form NH_4^+ . As NH_3 is removed, Ag^+ ions are released to solution, which can then react with Cl^- to reform AgCl(s) . The equations are $\text{Ag}(\text{NH}_3)_2^+\text{(aq)} + 2\text{H}^+\text{(aq)} \rightarrow \text{Ag}^+\text{(aq)} + 2\text{NH}_4^+\text{(aq)}$ and $\text{Ag}^+\text{(aq)} + \text{Cl}^-\text{(aq)} \rightarrow \text{AgCl(s)}$. 27. $[\text{Co}(\text{NH}_3)_6]\text{I}_3$: 3 mol AgI ; $[\text{Pt}(\text{NH}_3)_4]\text{I}_2$: 2 mol AgI ; $\text{Na}_2[\text{PtI}_6]$: 0 mol AgI ; $[\text{Cr}(\text{NH}_3)_4]\text{I}_2$: 1 mol AgI . 29. a. pentaamminechlororuthenium(III) ion; b. hexacyanoferrate(II) ion; c. tris(ethylenediamine)manganese(II) ion; d. pentaamminenitrocobalt(III) ion 31. a. hexaamminecobalt(II) chloride; b. hexaaquacobalt(III) iodide; c. potassium tetrachloroplatinate(II); d. potassium hexachloroplatinate(II); e. pentaamminechlorocobalt(III) chloride; f. triamminetritrocobalt(III) 33. a. $\text{K}_2[\text{CoCl}_4]$; b. $[\text{Pt}(\text{H}_2\text{O})(\text{CO})_3]\text{Br}_2$; c. $\text{Na}_3[\text{Fe}(\text{CN})_2(\text{C}_2\text{O}_4)_2]$; d. $[\text{Cr}(\text{NH}_3)_3\text{Cl}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)]_2$



37.  en = $\text{N}=\text{N}=\text{NH}, \text{CH}_2, \text{CH}_2, \text{NH}_2$



39. SCN^- , NO_2^- , and OCN^- can form linkage isomers; all are able to bond to the metal ion in two different ways. 41. $\text{Cr}(\text{acac})_3$ and *cis*- $\text{Cr}(\text{acac})_2(\text{H}_2\text{O})_2$ are optically active.



45. weak field 47. a. 0; b. 2; c. 2 49. The violet complex ion absorbs yellow-green light ($\lambda \approx 570$ nm), the yellow complex ion absorbs blue light ($\lambda \approx 450$ nm), and the green complex ion absorbs red light ($\lambda \approx 650$ nm). The violet complex ion is $\text{Cr}(\text{H}_2\text{O})_6^{3+}$, the yellow complex ion is $\text{Cr}(\text{NH}_3)_6^{3+}$, and the green complex ion is $\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2^+$. 51. CoBr_4^{2-} is a tetrahedral complex ion, while CoBr_6^{4-} is an octahedral complex ion. Since tetrahedral d -orbital splitting is less than one-half the octahedral d -orbital splitting, the octahedral complex ion (CoBr_6^{4-}) will absorb higher-energy light, which will have a shorter wavelength than 3.4×10^{-6} m ($E = hc/\lambda$). 53. 5 55. a. -11 kJ; b. $\Delta H^\circ = 172.5$ kJ; $\Delta S^\circ = 176$ J/K; $T > 980$. K 57. $[\text{Cr}(\text{NH}_3)_5\text{I}]_2$; octahedral 59. a. 2; b. 3; c. 4; d. 4 61. a. optical isomerism

- b.
- | | | |
|----|----|----|
| ↑↓ | ↑↓ | ↑↓ |
|----|----|----|
63. Octahedral Cr^{2+} complexes should be used. Cr^{2+} : $[\text{Ar}]3d^4$; High-spin (weak-field) Cr^{2+} complexes have four unpaired electrons and low-spin (strong-field) Cr^{2+} complexes have two unpaired electrons. Ni^{2+} : $[\text{Ar}]3d^8$; Octahedral Ni^{2+} complexes will always have two unpaired electrons, whether high or low spin. Therefore, Ni^{2+} complexes cannot be used to distinguish weak- from strong-field ligands by examining magnetic properties. Alternatively, the ligand field strengths can be measured using visible spectra. Either Cr^{2+} or Ni^{2+} complexes can be used for this method. 65. $\text{Pb}(\text{OH})_2$ will not form since Q is less than K_{sp} . 67. 60 69. a. -0.26 V; b. From standard reduction potentials, Co^{3+} ($\mathcal{E}^\circ = 1.82$ V) is a much stronger oxidizing agent than $\text{Co}(\text{en})_3^{3+}$ ($\mathcal{E}^\circ = -0.26$ V); c. In aqueous solution, Co^{3+} forms the hydrated transition metal complex, $\text{Co}(\text{H}_2\text{O})_6^{3+}$. In both complexes, $\text{Co}(\text{H}_2\text{O})_6^{3+}$ and $\text{Co}(\text{en})_3^{3+}$, cobalt exists as Co^{3+} , which has 6 d electrons. If we assume a strong-field case for each complex ion, then the d -orbital splitting diagram for each has the six electrons paired in the lower-energy t_{2g} orbitals. When each complex ion gains an electron, the electron enters the higher-energy e_g orbitals. Since en is a stronger-field ligand than H_2O , then the d -orbital splitting is larger for $\text{Co}(\text{en})_3^{3+}$, and it takes more energy to add an electron to $\text{Co}(\text{en})_3^{3+}$ than to $\text{Co}(\text{H}_2\text{O})_6^{3+}$. Therefore, it is more favorable for $\text{Co}(\text{H}_2\text{O})_6^{3+}$ to gain an electron than for $\text{Co}(\text{en})_3^{3+}$ to gain an electron. 71. No, since in all three cases six bonds are formed between Ni^{2+} and nitrogen. So ΔH values should be similar. ΔS° for formation of the complex ion is most negative for 6 NH_3 molecules reacting with a metal ion (7 independent species become 1). For penten reacting with a metal ion, 2 independent species become 1, so ΔS° is the least negative. Thus the chelate effect occurs because the more bonds a chelating agent can form to the metal, the more favorable ΔS° is for the formation of the complex ion, and the larger the formation constant.

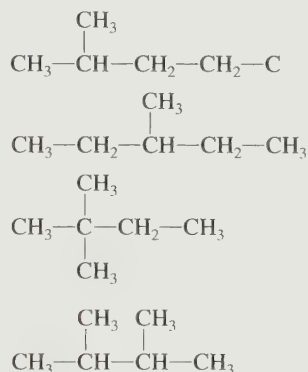
73. — d_{z^2}
 — $d_{x^2-y^2}, d_{xy}$
 — d_{xz}, d_{yz}

Chapter 22

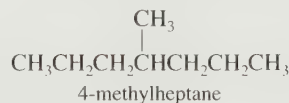
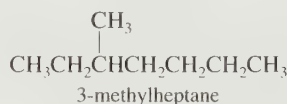
1. A consecutive chain of C atoms. They are not all in a true straight line since the bond angles at each carbon are 109.5° . 3. Resonance: All atoms are in the same position. Only the position of π electrons are different. Isomerism: Atoms are in different locations in space. Isomers are distinctly different substances. Resonance is the use of more than one Lewis structure to describe the bonding in a single compound. Resonance structures are not isomers. 5. Substitution: an atom or group is replaced by another atom or group; e.g., H in benzene is replaced by Cl: $\text{C}_6\text{H}_6 + \text{Cl}_2 \xrightarrow{\text{Catalyst}}$

$\text{C}_6\text{H}_5\text{Cl} + \text{HCl}$; addition: atoms or groups are added to a molecule; e.g., Cl_2 adds to ethene: $\text{CH}_2=\text{CH}_2 + \text{Cl}_2 \rightarrow \text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$ 7. A thermoplastic polymer can be remelted; a thermoset polymer cannot be softened once it is formed. 9. Crosslinking makes a polymer more rigid. 11. In nylon, hydrogen bonding interactions occur due to the presence of $[\text{N}-\text{H}]$ bonds in the polymer. For a given polymer chain length, there are more $[\text{N}-\text{H}]$ groups in nylon-46 as compared to nylon-6. Hence, nylon-46 forms a stronger polymer as compared to nylon-6 due to the increased hydrogen bonding interactions. 13. Primary: the amino acid sequence in the protein. The covalent bonds (peptide linkages) between amino acids maintain the primary structure. Secondary: includes structural features known as α -helix or pleated sheet. Both are maintained mostly through hydrogen bonding interactions. Tertiary: the overall shape of a protein, long and narrow or globular. Maintained by hydrophobic and hydrophilic interactions, such as salt linkages, hydrogen bonds, disulfide linkages, and dispersion forces. 15. All amino acids can act as both a weak acid and a weak base; this ability is the requirement for a buffer. The weak acid is the carboxylic end of the amino acid, and the weak base is the amine end of the amino acid. 17. Hydrogen bonding interactions occur between water and the many $[-\text{OH}]$ groups on starch. 19. nitrogen atoms with lone pairs of electrons 21. A deletion may change the entire code for a protein. A substitution will change only one single amino acid in a protein.

23. $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$

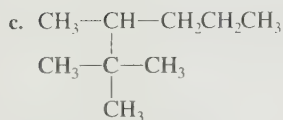
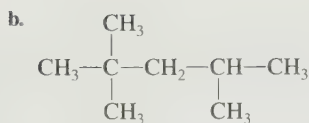


25. a. CH_3
 $\text{CH}_3\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
 2-methylheptane



- b. CH_3 CH_3
 $\text{CH}_3-\text{C}-\text{C}-\text{CH}_3$
 $| \quad |$
 $\text{CH}_3 \quad \text{CH}_3$
 2,2,3,3-tetramethylbutane

27. a. $\text{CH}_3-\text{CH}-\text{CH}_2-\text{CH}_2\text{CH}_3$
 $|$
 CH_3

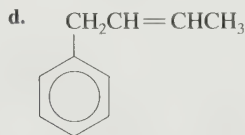
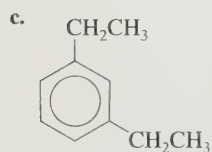
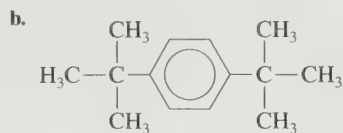
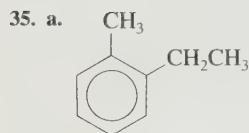
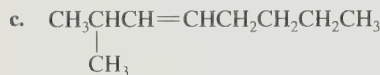


d. 2,2,3-trimethylhexane

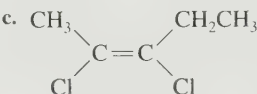
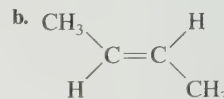
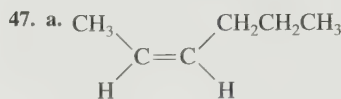
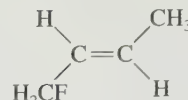
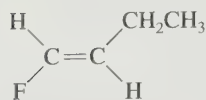
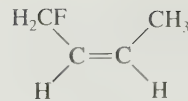
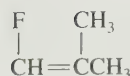
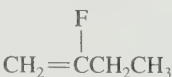
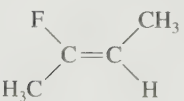
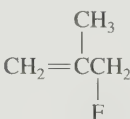
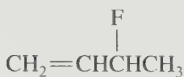
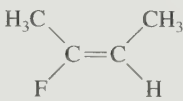
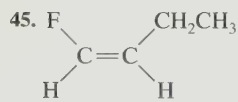
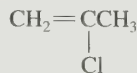
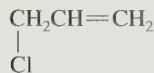
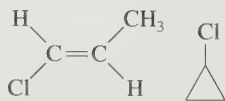
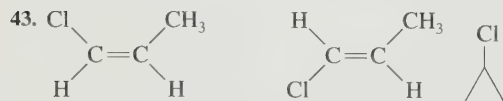
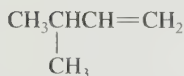
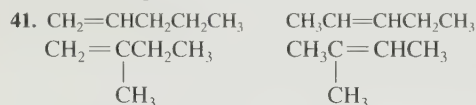
29. a. 2,2,4-trimethylhexane; b. 5-methylnonane; c. 2,2,4,4-tetramethylpentane; d. 3-ethyl-3-methyloctane 31. a. 1-butene;

b. 4-methyl-2-hexene; c. 2,5-dimethyl-3-heptene

33. a. $\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}_3$; b. $\text{CH}_3\text{CH}=\text{CHCH}=\text{CHCH}_2\text{CH}_3$;

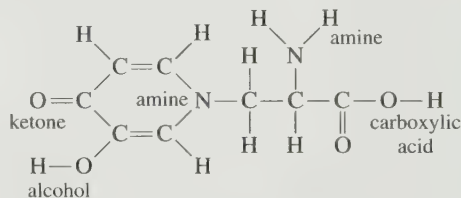


37. a. 1,3-dichlorobutane; b. 1,1,1-trichlorobutane; c. 2,3-dichloro-2,4-dimethylhexane; d. 1,2-difluoroethane; 39. [31], compounds b and c; [33], all compounds



49. a. 3 monochloro isomers of *n*-pentane; b. 4 monochloro isomers of 2-methylbutane; c. 3 monochloro isomers of 2,4-dimethylpentane; d. 4 monochloro isomers of methylcyclobutane 51. a. ketone; b. aldehyde; c. carboxylic acid; d. amine

53. a.

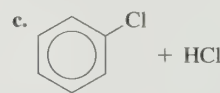
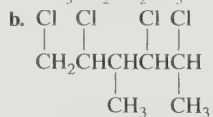


b. 5 carbons in ring and the carbon in $-\text{CO}_2\text{H}$; sp^2 ; the other two carbons: sp^3 ; c. 24 sigma bonds, 4 pi bonds 55. a. 3-chloro-1-butanol, primary;

b. 3-methyl-3-hexanol, tertiary; c. 2-methylcyclopentanol, secondary

57. 1-pentanol; 2-pentanol; 3-pentanol; 2-methyl-1-butanol; 2-methyl-2-butanol; 3-methyl-2-butanol; 3-methyl-1-butanol; 2,2-dimethyl-1-propanol; 6 ethers 59. a. 4,5-dichloro-3-hexanone; b. 2,3-dimethylpentanal; c. 3-methylbenzaldehyde or *m*-methylbenzaldehyde

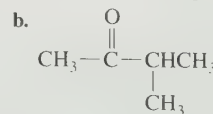
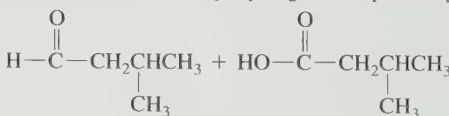
61. a. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$



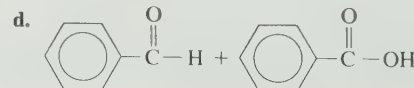
d. $\text{C}_4\text{H}_8(\text{g}) + 6\text{O}_2(\text{g}) \rightarrow 4\text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(\text{g})$

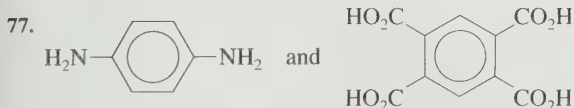
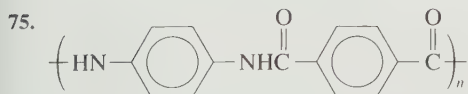
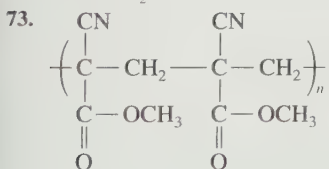
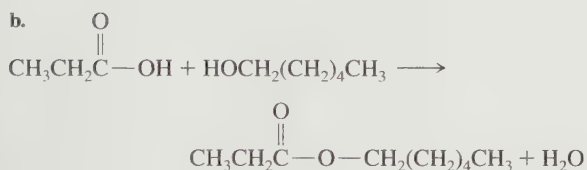
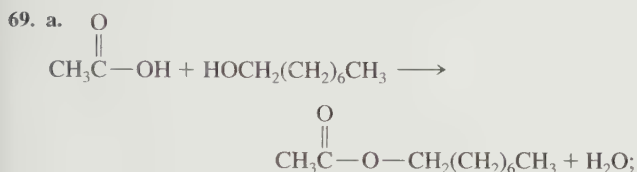
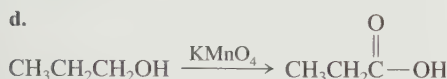
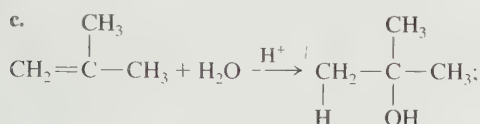
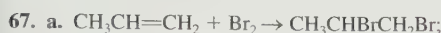
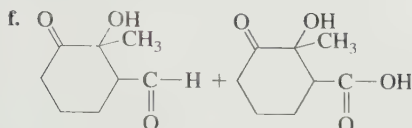
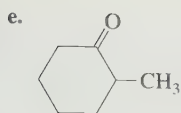
63. For the iron-catalyzed reaction, one of the *ortho* or *para* hydrogens in benzene is replaced by chlorine. When an iron catalyst is not present, then the benzene hydrogens are unreactive, which is seen for the light-catalyzed reaction where one of the methyl hydrogens is replaced by chlorine.

65. a.

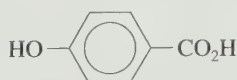


c. No reaction



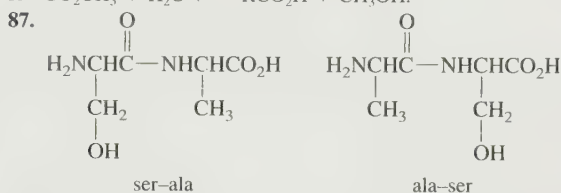


79. Divinylbenzene inserts itself into two adjacent polymer chains and bonds them together. The chains cannot move past each other because of the crosslinks making the polymer more rigid. 81. a. The polymer from 1,2-diaminoethane and terephthalic acid is stronger because of the possibility of hydrogen bonding between chains. b. The polymer of

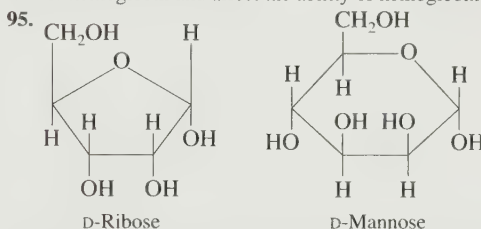


is more rigid because the chains are stiffer due to the rigid benzene rings in the chains. c. Polyacetylene is $n\text{HC}\equiv\text{CH} \rightarrow (\text{CH}=\text{CH})_n$. Polyacety-

lene is more rigid because the double bonds in the chains make the chains stiffer. 83. a. serine; tyrosine; threonine; b. aspartic acid; glutamic acid; c. histidine; lysine; arginine; tryptophan; d. glutamine; asparagine 85. a. aspartic acid and phenylalanine; b. Aspartame contains the methyl ester of phenylalanine. This ester can hydrolyze to form methanol, $\text{R}-\text{CO}_2\text{CH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{RCO}_2\text{H} + \text{CH}_3\text{OH}$.

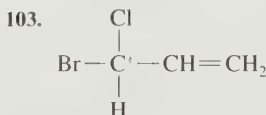
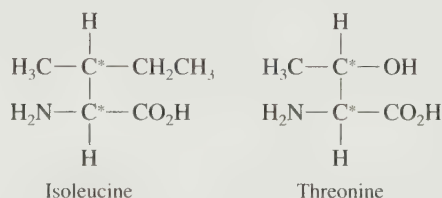


89. a. Six tetrapeptides are possible. From NH_2 to CO_2H end: phe-phe-gly-gly, gly-gly-phe-phe, gly-phe-phe-gly, phe-gly-gly-phe, phe-gly-phe-gly, gly-phe-gly-phe. b. Twelve tetrapeptides are possible. From NH_2 to CO_2H end: phe-phe-gly-ala, phe-phe-ala-gly, phe-gly-phe-ala, phe-gly-ala-phe, phe-ala-phe-gly, phe-ala-gly-phe, gly-phe-phe-ala, gly-phe-ala-phe, gly-ala-phe-phe, ala-phe-phe-gly, ala-phe-gly-phe, ala-gly-phe-phe. 91. Ionic: his, lys, or arg with asp or glu; hydrogen bonding: ser, glu, tyr, his, arg, asn, thr, asp, gln, or lys with any amino acid; covalent: cys with cys; London dispersion: all amino acids with nonpolar R groups (gly, ala, pro, phe, ile, trp, met, leu, val); dipole-dipole: tyr, thr, and ser with each other. 93. Glutamic acid has a polar R group and valine has a nonpolar R group. The change in polarity of the R groups could affect the tertiary structure of hemoglobin and affect the ability of hemoglobin to bond to oxygen.



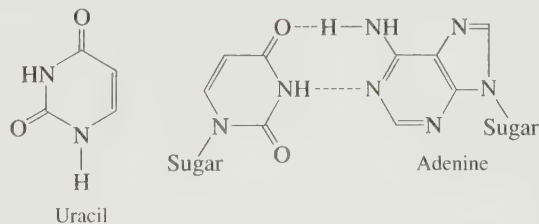
97. aldohexose: glucose, mannose, galactose; aldopentose: ribose, arabinose; ketohexose: fructose; ketopentose: ribulose 99. They differ in the orientation of a hydroxy group on a particular carbon. Starch is composed from α -D-glucose, and cellulose is composed from β -D-glucose.

101. The chiral carbons are marked with asterisks.

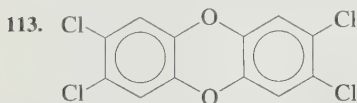


is optically active. The chiral carbon is marked with an asterisk.

105. C-C-A-G-A-T-A-T-G 107. Uracil will H-bond to adenine.

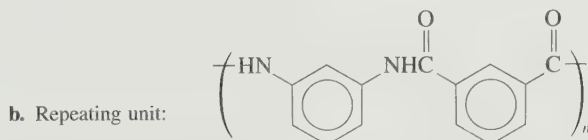
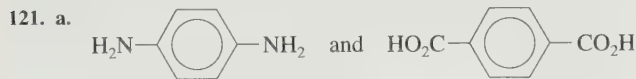


109. a. glu: CTT, CTC; val: CAA, CAG, CAT, CAC; met: TAC; trp: ACC; phe: AAA, AAG; asp: CTA, CTG; **b.** ACC-CTT-AAA-TAC or ACC-CTC-AAA-TAC or ACC-CTT-AAG-TAC or ACC-CTC-AAG-TAC; **c.** four (see answer in part b); **d.** met-asp-phe **e.** TAC-CTA-AAG; TAC-CTA-AAA; TAC-CTG-AAA **111.** $\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$, 1,2-dichloroethane; there is free rotation about the C—C single bond, which doesn't lead to different compounds. $\text{CHCl}=\text{CHCl}$, 1,2-dichloroethene; there is no rotation about the C=C double bond. This creates the *cis* and *trans* isomers, which are different compounds.

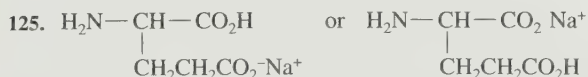


There are many possibilities for isomers. Any structure with four chlorines replacing four hydrogens in any of the numbered positions would be an isomer; i.e., 1,2,3,4-tetrachloro-dibenzo-*p*-dioxin is a possible isomer.

115. Alcohols consist of two parts, the polar OH group and the nonpolar hydrocarbon chain attached to the OH group. As the length of the nonpolar hydrocarbon chain increases, the solubility of the alcohol decreases. In methyl alcohol (methanol), the polar OH group can override the effect of the nonpolar CH_3 group, and methyl alcohol is soluble in water. In stearyl alcohol, the molecule consists mostly of the long nonpolar hydrocarbon chain, so it is insoluble in water. **117.** *n*-hexane, 69°C; pentanal, 103°C; 1-pentanol, 137°C; butanoic acid, 164°C. **119.** 1-butene

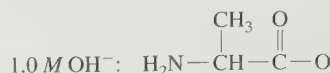
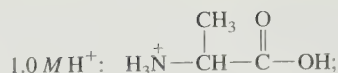


The two polymers differ in the substitution pattern on the benzene rings. The Kevlar chain is straighter, and there is more efficient hydrogen bonding between Kevlar chains than between Nomex chains. **123. a.** The bond angles in the ring are about 60°. VSEPR predicts bond angles close to 109°. The bonding electrons are much closer together than they prefer, resulting in strong electron-electron repulsions. Thus ethylene oxide is unstable (reactive). **b.** The ring opens up during polymerization and the monomers link together through the formation of O—C bonds.

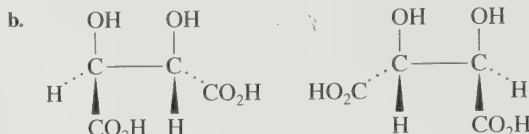


The first structure is MSG, which is impossible for you to predict. **127.** In the reaction, P—O and O—H bonds are broken and P—O and O—H bonds are formed. Thus $\Delta H \approx 0$. $\Delta S < 0$, since two molecules are going to form one molecule. Thus $\Delta G > 0$, not spontaneous.

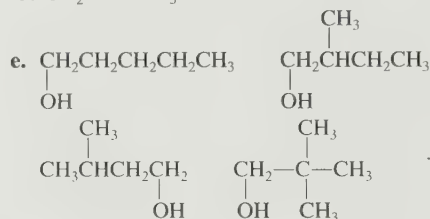
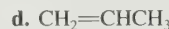
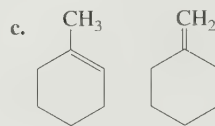
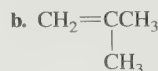
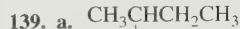
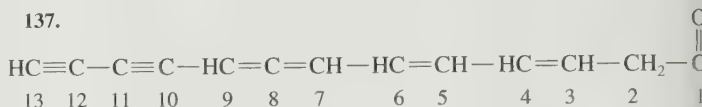
129.



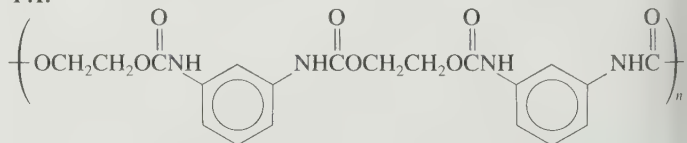
131. The Cl^- ions are lost upon binding to DNA. The dimension is just right for cisplatin to bond to two adjacent bases in one strand of the helix, which inhibits DNA synthesis. **133.** 6.07 **135. a.** No; the mirror image is superimposable.



137.



141.



143. a. The temperature of the rubber band increases when it is stretched; **b.** exothermic (heat is released); **c.** As the chains are stretched, they line up more closely resulting in stronger dispersion forces between the chains. Heat is released as the strength of the intermolecular forces increases. **d.** ΔG is positive and ΔS is negative; **e.** The structure of the stretched polymer chains is more ordered than in unstretched rubber. Disorder decreases as the rubber band is stretched.

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Group numbers 1–18 represent the system recommended by the International Union of Pure and Applied Chemistry.

Table of Atomic Masses*

Element	Symbol	Atomic Number	Atomic Mass	Element	Symbol	Atomic Number	Atomic Mass	Element	Symbol	Atomic Number	Atomic Mass
Actinium	Ac	89	[227] [§]	Hafnium	Hf	72	178.5	Promethium	Pm	61	[145]
Aluminum	Al	13	26.98	Hassium	Hs	108	[265]	Protactinium	Pa	91	[231]
Americium	Am	95	[243]	Helium	He	2	4.003	Radium	Ra	88	226
Antimony	Sb	51	121.8	Holmium	Ho	67	164.9	Radon	Rn	86	[222]
Argon	Ar	18	39.95	Hydrogen	H	1	1.008	Rhenium	Re	75	186.2
Arsenic	As	33	74.92	Indium	In	49	114.8	Rhodium	Rh	45	102.9
Astatine	At	85	[210]	Iodine	I	53	126.9	Rubidium	Rb	37	85.47
Barium	Ba	56	137.3	Iridium	Ir	77	192.2	Ruthenium	Ru	44	101.1
Berkelium	Bk	97	[247]	Iron	Fe	26	55.85	Rutherfordium	Rf	104	[261]
Beryllium	Be	4	9.012	Krypton	Kr	36	83.80	Samarium	Sm	62	150.4
Bismuth	Bi	83	209.0	Lanthanum	La	57	138.9	Scandium	Sc	21	44.96
Bohrium	Bh	107	[264]	Lawrencium	Lr	103	[260]	Seaborgium	Sg	106	[263]
Boron	B	5	10.81	Lead	Pb	82	207.2	Selenium	Se	34	78.96
Bromine	Br	35	79.90	Lithium	Li	3	6.941	Silicon	Si	14	28.09
Cadmium	Cd	48	112.4	Lutetium	Lu	71	175.0	Silver	Ag	47	107.9
Calcium	Ca	20	40.08	Magnesium	Mg	12	24.31	Sodium	Na	11	22.99
Californium	Cf	98	[251]	Manganese	Mn	25	54.94	Strontium	Sr	38	87.62
Carbon	C	6	12.01	Meitnerium	Mt	109	[268]	Sulfur	S	16	32.07
Cerium	Ce	58	140.1	Mendelevium	Md	101	[258]	Tantalum	Ta	73	180.9
Cesium	Cs	55	132.90	Mercury	Hg	80	200.6	Technetium	Tc	43	[98]
Chlorine	Cl	17	35.45	Molybdenum	Mo	42	95.94	Tellurium	Te	52	127.6
Chromium	Cr	24	52.00	Neodymium	Nd	60	144.2	Terbium	Tb	65	158.9
Cobalt	Co	27	58.93	Neon	Ne	10	20.18	Thallium	Tl	81	204.4
Copper	Cu	29	63.55	Neptunium	Np	93	[237]	Thorium	Th	90	232.0
Curium	Cm	96	[247]	Nickel	Ni	28	58.69	Thulium	Tm	69	168.9
Dubnium	Db	105	[262]	Niobium	Nb	41	92.91	Tin	Sn	50	118.7
Dysprosium	Dy	66	162.5	Nitrogen	N	7	14.01	Titanium	Ti	22	47.88
Einsteinium	Es	99	[252]	Nobelium	No	102	[259]	Tungsten	W	74	183.9
Erbium	Er	68	167.3	Osmium	Os	76	190.2	Uranium	U	92	238.0
Europium	Eu	63	152.0	Oxygen	O	8	16.00	Vanadium	V	23	50.94
Fermium	Fm	100	[257]	Palladium	Pd	46	106.4	Xenon	Xe	54	131.3
Fluorine	F	9	19.00	Phosphorus	P	15	30.97	Ytterbium	Yb	70	173.0
Francium	Fr	87	[223]	Platinum	Pt	78	195.1	Yttrium	Y	39	88.91
Gadolinium	Gd	64	157.3	Plutonium	Pu	94	[244]	Zinc	Zn	30	65.38
Gallium	Ga	31	69.72	Polonium	Po	84	[209]	Zirconium	Zr	40	91.22
Germanium	Ge	32	72.59	Potassium	K	19	39.10				
Gold	Au	79	197.0	Praseodymium	Pr	59	140.9				

*The values given here are to four significant figures where possible. [§]A value given in parentheses denotes the mass of the longest-lived isotope.

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Physical Constants

Constant	Symbol	Value
Atomic mass unit	amu	$1.66054 \times 10^{-27} \text{ kg}$
Avogadro's number	N	$6.02214 \times 10^{23} \text{ mol}^{-1}$
Bohr radius	a_0	$5.292 \times 10^{-11} \text{ m}$
Boltzmann constant	k	$1.38066 \times 10^{-23} \text{ J/K}$
Charge of an electron	e	$1.60218 \times 10^{-19} \text{ C}$
Faraday constant	F	$96,485 \text{ C/mol}$
Gas constant	R	$8.31451 \text{ J/K} \cdot \text{mol}$ $0.08206 \text{ L} \cdot \text{atm/K} \cdot \text{mol}$
Mass of an electron	m_e	$9.10939 \times 10^{-31} \text{ kg}$ $5.48580 \times 10^{-4} \text{ amu}$
Mass of a neutron	m_n	$1.67493 \times 10^{-27} \text{ kg}$ 1.00866 amu
Mass of a proton	m_p	$1.67262 \times 10^{-27} \text{ kg}$ 1.00728 amu
Planck's constant	h	$6.62608 \times 10^{-34} \text{ J} \cdot \text{s}$
Speed of light	c	$2.99792458 \times 10^8 \text{ m/s}$



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